

APPENDIX A

Reprints of OH Rate Constant Determination and Reactivity Scale Papers

Relative Rate Constants for Reaction of the Hydroxyl Radical with a Series of Alkanes, Alkenes, and Aromatic Hydrocarbons

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The relative rates of disappearance in air at 305 ± 2 K of a set of 14 alkanes, alkenes, and aromatic hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. The observed rates of disappearance were used to derive relative rates of reaction with the hydroxyl radical (OH) on the previously validated basis that OH is the species dominantly responsible for the hydrocarbon disappearance under the experimental conditions employed. Absolute rate constants, obtained from the relative values by using the mean of the published rate constants for OH + *n*-butane ($1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), are ($k \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$): isopentane, 2.0 ± 0.4 ; 2-methylpentane, 3.2 ± 0.6 ; 3-methylpentane, 4.3 ± 0.9 ; *n*-hexane, 3.8 ± 0.8 ; *m*-xylene, 12.9 ± 2.6 ; *n*-propylbenzene, 3.7 ± 0.8 ; isopropylbenzene, 3.7 ± 0.8 ; ethylbenzene, 4.8 ± 1.0 ; *o*-ethyltoluene, 8.2 ± 1.6 ; *m*-ethyltoluene, 11.7 ± 2.3 ; *p*-ethyltoluene, 7.8 ± 1.6 ; ethene, 5.2 ± 1.0 ; propene, 17.5 ± 3.5 ; *cis*-2-butene, 39.2 ± 8.0 ; 1,3-butadiene, 46.4 ± 9.3 . In the case of seven of the compounds investigated these results are shown to be in good agreement with literature values reported for elementary rate constant determinations. For the remaining seven compounds no previous determinations have been made.

Introduction

The hydroxyl radical is well known to be an important species in the chemistry of combustion systems,^{1,2} the stratosphere,³⁻⁵ and the troposphere.⁶⁻⁹ Recent direct determinations of its concentration in ambient air^{10,11} have

shown average daytime levels of about 5×10^6 molecule cm^{-3} in good agreement with predictions from computer models of the formation of photochemical air pollution.^{6,12-14}

In order to develop satisfactory chemical mechanisms for modeling combustion and photooxidation systems includ-

ing urban airshed models,^{15,16} kinetic data for the reactions of the OH radical with hydrocarbons, as well as various inorganic species, are necessary. Prior to 1970 relatively few absolute rate constants were available for OH reactions with organic species; however, since then a large number of determinations have been reported for alkanes¹⁷⁻²⁷ and alkenes.^{21-23,28-36} Although aromatic compounds such as toluene, xylenes, propylbenzene, *m*-ethyltoluene, and 1,2,3- and 1,2,4-trimethylbenzenes are present in polluted ambient air,³⁷⁻³⁹ only in the past few years have significant studies been reported on the reactions of the OH radical with some of these aromatics.^{21,40-42} For example, recently we reported the use of an environmental chamber to obtain accurate relative rate constants for the gas phase reaction of hydroxyl radicals with a series of aromatic hydrocarbons using *n*-butane as the reference compound.⁴² Although a number of other species are present in these experiments (i.e., O(³P), HO₂, O₃, NO₃, etc.), with the exception of O₃ in the case of the alkenes, these species have been shown to make at most minor contributions to the observed disappearance of the hydrocarbons investigated. Thus, the rate constants determined in our previous study⁴² are in good agreement with those determined subsequently in separate studies of the reactions of individual compounds with OH using a flash photolysis-resonance fluorescence technique.^{40,41}

On the basis of this validation of the environmental chamber method, we have extended our investigation to include an additional six aromatic hydrocarbons, four alkanes, and four alkenes.

Experimental Section

Irradiations of the HC-NO_x-air system were carried out in an all-glass (Pyrex) chamber of approximately 6400-l. volume equipped with two externally mounted, diametrically opposed banks of Sylvania 40 BL fluorescent lamps.⁴³ Before each experiment the chamber was flushed for a minimum of 2 h at a rate of 12-15 scfm with a purified air stream.⁴⁴ The resulting matrix air contained less than $\sim 1 \times 10^{-9}$ M (100 ppb C) of nonmethane hydrocarbons. All reactants were injected into the chamber using 100-ml precision bore syringes and rapid mixing was obtained using Teflon-coated sonic pumps. During irradiation, the chamber temperature was maintained at 305 ± 2 K by passing chilled air between the chamber walls and the fluorescent lamp banks.

Hydrocarbon disappearance was measured by gas chromatography using the columns and techniques developed by Stephens and Burleson.^{37,45} Ozone⁴⁶ was monitored by means of ultraviolet absorption (Dasibi Model 1003 analyzer), carbon monoxide by gas chromatography (Beckman 6800 Air Quality analyzer), and NO-NO₂-NO_x by the chemiluminescent reaction of NO with ozone (TECO Model 14B).

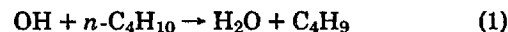
The concentrations of the reactants ranged between 4.5 and 9.0×10^{-10} M (11-22 ppb in air) except for ethene, ethane, acetylene, and *n*-butane whose concentrations were 1.8, 3.7, 1.8, and 8.3×10^{-9} M (45, 92, 45, and 203 ppb in air), respectively. In addition low concentrations of carbonyl compounds (formaldehyde, acetaldehyde, and acetone) were present. Initial concentrations in the photolysis experiments were 27×10^{-9} M (2900 ppb C) of total nonmethane hydrocarbons, 1.75×10^{-9} M (0.43 ppm) of NO_x (with an NO₂/NO_x ratio of 0.12), 28.5×10^{-9} M (7 ppm) of CO, and 112.9×10^{-9} M (2775 ppb) of methane together

with water at 50% relative humidity. Four replicate experiments were carried out in which this mixture was irradiated for 3 h with continuous analysis of inorganic species and analysis of hydrocarbons every hour. The irradiation period was extended from 2 to 3 h compared with our earlier study in order to obtain additional data points. The light intensity, measured as the rate of NO₂ photolysis in nitrogen, k_1 ,⁴⁷ was approximately 0.26 min^{-1} . All data were corrected for losses due to sampling from the chamber (0.9-2.0%/h) by subtraction of the average dilution rate from the observed hydrocarbon disappearance rate. Although the HC/NO_x ratio was chosen to delay the formation of ozone, after 3 h of irradiation the ozone concentration was 0.065×10^{-9} M (0.016 ppm) or less in three of the runs and 0.13×10^{-9} M (0.031 ppm) in the fourth (which had a higher initial formaldehyde concentration). A small correction for loss of hydrocarbon due to reaction with ozone was applied to the alkene disappearance rates.

Results

The rates of disappearance observed during a 3-h run for the seven aromatic hydrocarbons, four alkanes, and four alkenes are shown in Figures 1-3, respectively (*n*-butane is included as the reference compound in each figure). Table I gives the disappearance rates for these reactants (after application of the dilution correction and for alkenes, the ozone correction), relative to that for *n*-butane, based on data from the four separate experiments.

With the assumption that the OH radical is the species responsible for the hydrocarbon depletion during the 3-h irradiation, absolute rate constants were derived from the relative rates of disappearance using a value of $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as the mean of the existing literature values for the reaction of OH with *n*-butane^{21,23,24,27}



These results are shown in Table I and are compared with existing literature values whenever possible in Table II.

Discussion

As seen from Table II, the validation of the assumption that the OH radical is by far the major species depleting the hydrocarbons (during the first 2-3 h of reaction) has been provided by the good agreement observed between OH rate constants determined in our previous chamber study⁴² for benzene, toluene, *o*-, *m*-, and *p*-xylenes, and the trimethylbenzenes with those determined in elementary reaction studies of each individual hydrocarbon.^{40,41} The extent to which this assumption is valid is indicated by the results of computer modeling calculations⁴⁸ (shown in Figure 4) for an HC-NO_x system of overall concentrations identical with that used in this study. In the computer simulation a propene and *n*-butane mixture was used as a surrogate for the complex hydrocarbon mixture employed in the experiment and the rate of attack on propene by OH, O₃, O(³P), and HO₂ was calculated. The relative and total concentrations of propene and *n*-butane were chosen such that the overall hydrocarbon reactivity toward the OH radical would equal that predicted for the complex mixture. It is clear from Figure 4 that, although OH is the major attacking species in these experiments, the O₃ contribution to the disappearance rates of the alkenes increases with time of irradiation. In contrast the rates of reaction of O₃ with alkanes and aromatics are many orders of magnitude slower⁵⁰⁻⁵² than with alkenes^{49,53} and no correction for

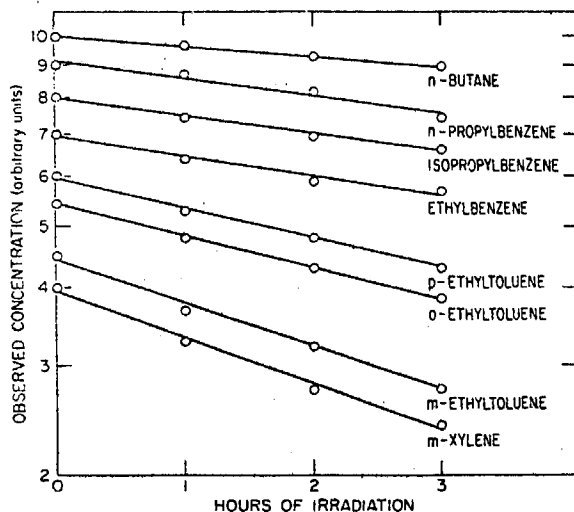


Figure 1. Logarithm of the aromatic hydrocarbon concentration during 3-h photolysis of HC-NO_x mixture in air at 305 ± 2 K and 1 atm.

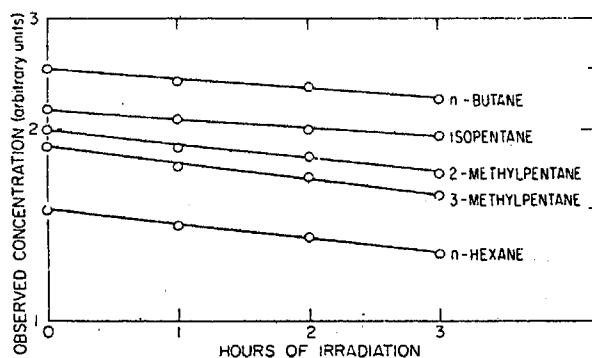


Figure 2. Logarithm of concentrations of alkanes during 3-h photolysis of HC-NO_x mixture in air at 305 ± 2 K and 1 atm.

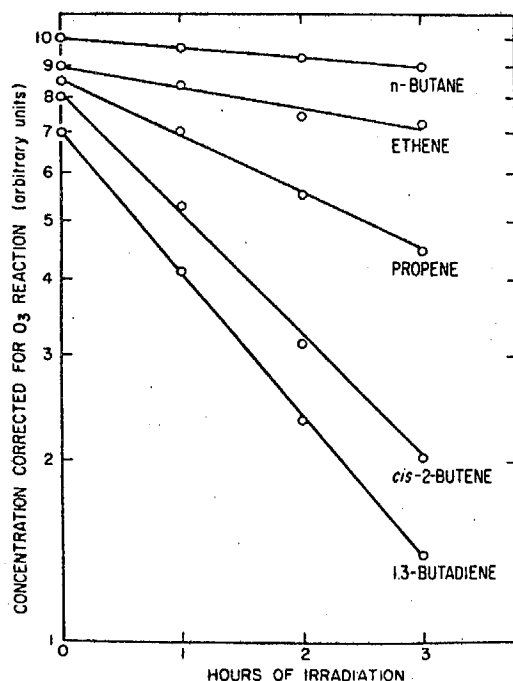


Figure 3. Logarithm of concentrations of alkenes during 3-h photolysis of HC-NO_x mixture in air at 305 ± 2 K and 1 atm.

TABLE I: Rates of Disappearance and Rate Constants for Selected Alkanes, Alkenes, and Aromatic Hydrocarbons at 1 atm in Air at 305 ± 2 K

Compound	Relative rate of disappearance	$10^{-9}k, ^\circ \text{M}^{-1} \text{s}^{-1}$
<i>n</i> -Butane	1	1.8 ^b
Isopentane	1.10	2.0 ± 0.4
2-Methylpentane	1.77	3.2 ± 0.6
3-Methylpentane	2.40	4.3 ± 0.9
<i>n</i> -Hexane	2.09	3.8 ± 0.8
<i>m</i> -Xylene	7.18	12.9 ± 2.6
<i>n</i> -Propylbenzene	2.07	3.7 ± 0.8
Isopropylbenzene	2.03	3.7 ± 0.8
Ethylbenzene	2.65	4.8 ± 1.0
<i>o</i> -Ethyltoluene	4.57	8.2 ± 1.6
<i>m</i> -Ethyltoluene	6.49	11.7 ± 2.3
<i>p</i> -Ethyltoluene	4.33	7.8 ± 1.6
Ethene	2.88	5.2 ± 1.0
Propene	9.70	17.5 ± 3.5
1,3-Butadiene	25.8	46.4 ± 9.3
<i>cis</i> -2-Butene	21.8	39.2 ± 8.0

^a The indicated error limits are ±20% and are the estimated overall error limits. ^b Placed on an absolute basis using the mean of the literature values; ref 21, 23, 24, and 27.

TABLE II: Rate Constants, k , for OH Radical Reactions with *n*-Butane and Selected Alkane, Alkenes, and Aromatic Hydrocarbons at Room Temperature

Compound	$10^{-9}k, \text{M}^{-1} \text{s}^{-1}$	
	Environmental chamber studies ^{a,b}	Lit. values
Benzene	≤2.3 ^a	0.74 ± 0.07 ^c 0.95 ± 0.07 ^d
Toluene	2.5 ± 0.9 ^a	3.47 ± 0.35 ^c 3.67 ± 0.24 ^d
<i>o</i> -Xylene	7.7 ± 2.3 ^a	9.18 ± 0.90, ^c 11 ^e
<i>m</i> -Xylene	14 ± 1 ^a	14.2 ± 1.4 ^c
<i>p</i> -Xylene	12.9 ± 2.6 ^b	11 ^e
1,2,3-Trimethylbenzene	7.4 ± 1.5 ^a	7.32 ± 0.72, ^c 11 ^e
1,2,4-Trimethylbenzene	14 ± 3 ^a	15.8 ± 1.6 ^c
1,3,5-Trimethylbenzene	31 ± 4 ^a	28.3 ± 2.9 ^c
Isopentane	2.0 ± 0.4 ^b	2.7 ^f
2-Methylpentane	3.2 ± 0.6 ^b	3.4 ^f
3-Methylpentane	4.3 ± 0.9 ^b	3.4 ^f
<i>n</i> -Hexane	3.8 ± 0.8 ^b	2.9 ^f
Ethene	5.2 ± 1.0 ^b	5.7 ± 0.6 ^g 1.1, ^h 3.0, ⁱ 3.2 ± 0.4, ^j 3.0, ^k 1.8 ± 0.6 ^l 1.0 ± 0.3, ^m 1.3 ± 0.1 ⁿ
Propene	17.5 ± 3.5 ^b	21.7 ± 2.4 ^g 10.2 ± 2.6 ^h 8.7 ± 1.3, ⁱ 15.1 ± 1.5, ^o 9.6 ± 0.3, ^p 3.0 ± 1.0, ^m 3.0 ± 0.6 ⁿ
<i>cis</i> -2-Butene	39.2 ± 8.0 ^b	36.7, ^h 32.3 ± 3.2, ^o 25.7 ± 1.5 ^p

^a Reference 42. ^b From Table I. ^c Reference 40. ^d Reference 41.

^e Reference 21 for a mixture of xylene isomers. ^f Reference 24.

^g Reference 33. ^h References 30 and 21. ⁱ Reference 31. ^j Reference 36.

^k Reference 29. ^l Reference 28. ^m Reference 22. ⁿ Reference 32.

^o Reference 35. ^p Reference 34.

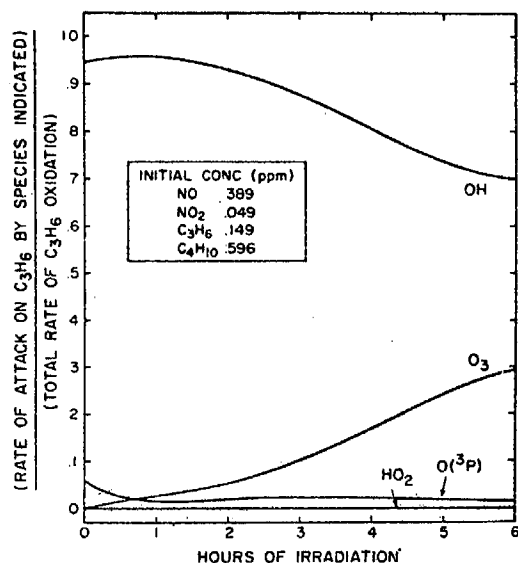
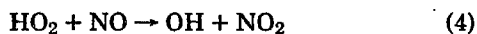
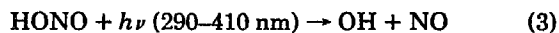
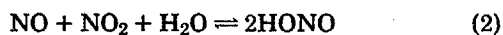


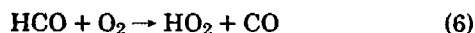
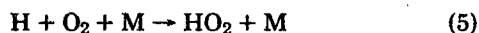
Figure 4. Predicted relative importance of several reactive intermediates during photooxidation of propene-*n*-butane mixture under simulated atmospheric conditions.

their reaction with ozone was necessary. For example, the rate constant for the reaction of ozone with toluene is about nine orders of magnitude lower than that for OH with toluene. During the initial hours of irradiation other species such as NO_3^{55} and HO_2^{56} may contribute slightly to hydrocarbon disappearance rates, especially for alkenes, but since their concentrations, and in some cases rate constants, are not known, correction was not possible.

Hydroxyl Radical Source in this System. The major sources of OH in our experimental system are probably the reactions^{7,8,13,15}



Nitrous acid has been observed in a chamber study of simulated atmospheres carried out in our laboratory⁵⁷ when a mixture of propene and nitrogen oxides in moist air was photolyzed, indicating that HONO can be formed in HC/ NO_x systems under conditions similar to those employed in the present study (Nash⁵⁸ claims to have measured HONO in ambient air, at levels up to 11 ppb). Direct evidence for formation of OH radicals in environmental chambers has been provided recently by Niki, Weinstock, and coworkers.^{11,54} Reaction 4, of major importance, provides a further source of the OH radical. HO_2 can be formed in air^{56,59} by any mechanism producing H atoms or formyl radicals via the reactions



Thus any mechanism producing HO_2 in our system is also a means of furnishing OH radicals via reaction 4.

The concentration of OH radicals present during these experiments was calculated to be $(1.5\text{--}2.0) \times 10^6$ molecules cm^{-3} using the observed rates of *m*-xylene disappearance (corrected for dilution) and the previously determined rate constant for OH + *m*-xylene.^{40,42} These concentrations are

of the same order as those observed directly in ambient air^{10,11} as discussed above.

Aromatic Hydrocarbons. Present results for the rate constant for the reaction of OH with *m*-xylene show good agreement with the previous study⁴² carried out in our laboratory (Table II), indicating good reproducibility for this technique.

Rate constants for the reaction of OH with the propylbenzenes and ethyltoluenes have not been reported previously. However, the trend in rate constants for the reaction with *o*-, *m*-, and *p*-ethyltoluene is identical with that previously determined for the xylenes^{40,42} which supports the concept that OH is an electrophilic species, since attack on the meta compound is favored.

Davis et al.⁴¹ have studied the reaction of OH with benzene and toluene and from the observed pressure dependence of the reactions, conclude that addition occurs at least 50% of the time. In an environmental chamber study similar to that reported here, Schwartz et al.⁶⁰ tentatively identified a number of aerosol products such as phenols and aromatic nitro compounds from the photooxidation of toluene in the presence of nitrogen oxides. A mechanism was proposed assuming initial addition of OH to the aromatic ring. In the case of the more highly substituted aromatic compounds studied here, it may be possible that hydrogen abstraction from the side chain could possibly be as important as addition. This is supported by the fact that a log plot of the OH-aromatic hydrocarbon rate constants vs. the ionization potential of the hydrocarbon (which, for abstraction reactions, is expected to be linear) in this case did not yield a straight line.

Detailed product studies are required in order to obtain the quantitative data necessary to further elucidate the mechanism of OH attack on various aromatic hydrocarbons.

Alkanes. Greiner²⁴ has derived an empirical formula for calculating the rates of reaction of OH with alkanes based on his experimental results for the reaction of the OH radical with selected alkanes:

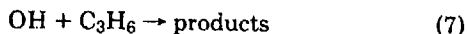
$$k = 6.15 \times 10^8 N_1 \exp(-1635/RT) \\ + 14.1 \times 10^8 N_2 \exp(-850/RT) \\ + 12.6 \times 10^8 N_3 \exp(+190/RT) \text{ M}^{-1} \text{ s}^{-1}$$

where N_1 , N_2 , and N_3 are the numbers of primary, secondary, and tertiary hydrogen atoms, respectively, in the alkane. We have used this equation to calculate the rate constants for isopentane, 2- and 3-methylpentane, and *n*-hexane. The calculated values are in quite good agreement with the experimental values. Although Greiner's formula predicts the same rate constants for the 2- and 3-methylpentanes, our study suggests that the latter is somewhat higher. Indeed this may be expected since the stability of the radical formed by the abstraction of the tertiary H atom from 3-methylpentane should be greater than that for the radical formed from similar attack in the 2-methylpentane case.

Alkenes. Unlike the alkanes and the aromatic compounds, alkenes react with ozone at a significant rate. Thus, in our experimental system, the small amounts of O_3 formed during the 3-h photolyses contributed to the alkene disappearance rates. From the measured concentrations of ozone and the published rate constants for the reaction of O_3 with the alkenes studied,^{49,53,61-63} a correction was made to the alkene disappearance rates for loss due to reaction with ozone. This amounted to ~3% for ethene, ~7% for

propene, ~21% for *cis*-2-butene, and ~2% for 1,3-butadiene.

Our results for the reaction of OH with propene

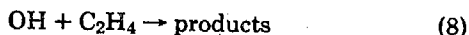


are within experimental error of a recent absolute determination of k_7 using flash photolysis-resonance fluorescence,³⁵ while the value of k_7 given in Table II for the result of Cox³³ incorporates a stoichiometry factor of 2 to 3. In parallel studies in this laboratory using flash photolysis-resonance fluorescence³⁵ no evidence was found within experimental error of a pressure effect for k_7 by varying the total pressure from 25 to 100 Torr of argon, but additional studies should be carried out, especially at lower pressures where such an effect would become evident, to see whether k_7 exhibits any pressure dependence.

The value of the rate constant obtained in this study for the reaction of OH with *cis*-2-butene, though somewhat high, is within experimental error of values previously reported from direct determinations.^{21,34,35} In this case a significant (21%) correction for reaction with O₃ had to be applied to the data.

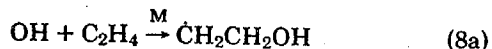
No previous determinations of absolute rate constants have been reported for the reaction of OH with 1,3-butadiene. However, the close agreement between our values for *cis*-2-butene and 1,3-butadiene is consistent with the work by Cvetanovic and Doyle⁶⁴ who showed that these two compounds reacted at similar rates with oxygen atoms.

The value obtained in this study for the rate constant of the reaction



of $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is about a factor of 2 higher than published values from low pressure (<300 Torr) studies.^{21,22,28-32,36} The only other study to date carried out at atmospheric pressure is that recently reported by Cox,³³ in which OH was generated by photolyzing gaseous nitrous acid in nitrogen/oxygen mixtures (2:1) at 760 Torr and the effect of added alkenes on the photolysis of nitrous acid was studied. A rate constant $\alpha k_8 = (5.7 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained relative to a value of $9.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of OH with CO, where α is a stoichiometry factor. Cox suggests that α is between 2 and 3 based on published values for the direct determination of k_8 . Davis et al.³⁶ have shown that the significant differences between low pressure measurements of reaction 8 can be rationalized by the fact that the reaction exhibits a pressure dependence over the region studied (3 to 300 Torr of He).

This pressure dependence is probably due to the initial formation of the adduct observed by Niki and coworkers.^{21,30} Presumably this adduct becomes stabilized by collisional deactivation



While it is possible that our determination of k_8 is higher than previous values due to the fact that species other than OH and O₃ are depleting the ethene, at least part of the discrepancy may be due to the difference in pressure regions studied. Figure 5 shows a plot of $\log k_8$ vs. $\log P$ where P is the total pressure in the system for studies carried out using N₂, O₂, or N₂O as diluent gases. Studies carried out using less efficient third body gases such as He are not plotted since the present study is focused on ambient atmospheric conditions and third bodies such as N₂ or the

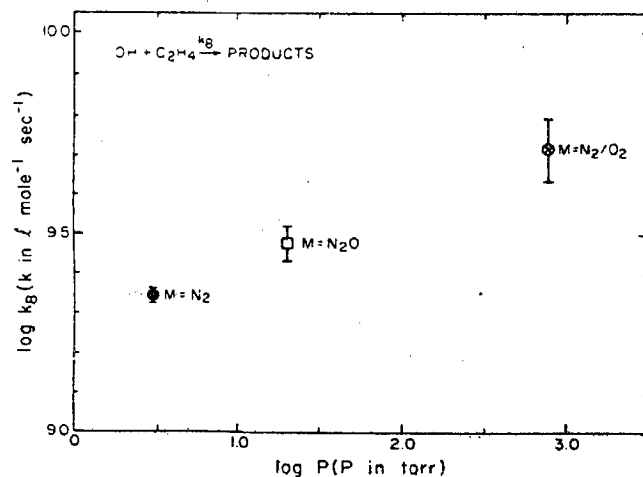


Figure 5. Variation with pressure of the rate constant k_8 for the reaction of OH with C₂H₄; M is "bath gas" in reaction 8: (●) Davis et al.,³⁶ (□) Smith and Zellner,³¹ (⊗) this work.

equivalent. Thus, at 3 Torr of diluent gas, the results of Davis et al.³⁶ differ by a factor of 1.6 depending on whether N₂ or He is used as the diluent gas. Although our results for ethene are subject to some uncertainty, it appears possible that reaction 8 is not at the limiting high pressure kinetics region until the pressure exceeds 1 atm.

Conclusions

Relative rate constants have been determined for the reaction of OH with 14 hydrocarbons and these rate constants have been placed on an absolute basis using the literature values for the rate constant of OH + *n*-butane. No previous determinations have been reported in the case of seven of these compounds.

Our results indicate that the reaction of OH with ethene possibly does not obey second-order kinetics until pressures exceed 1 atm while for propene and the higher alkenes the reactions are second order at atmospheric pressure.

The comparatively high rates of reaction observed for the aromatic hydrocarbons have significant implications for the control of photochemical air pollution. This subject and the use of the present data in the formulation of a hydrocarbon reactivity scale has been treated in detail elsewhere.⁶⁵

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Relative Rate Constants for the Reaction of the Hydroxyl Radical with Selected Ketones, Chloroethenes, and Monoterpene Hydrocarbons

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The relative rates of disappearance of three monoterpene hydrocarbons, two chloroethenes, and three aliphatic ketones were measured in an environmental chamber under simulated atmospheric conditions at 305 ± 2 K. The observed rates of disappearance were used to derive relative rates of reaction of these organic compounds with the hydroxyl radical (OH) on the previously validated basis that OH is the species dominantly responsible for the hydrocarbon disappearance under the experimental conditions employed. Absolute rate constants, obtained from the relative values using the published rate constant for OH + isobutene ($3.05 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), are ($k \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$): α -pinene, 3.5 ± 0.5 ; β -pinene, 4.1 ± 0.6 ; *d*-limonene, 9.0 ± 1.4 ; methyl ethyl ketone, 0.20 ± 0.06 ; methyl isobutyl ketone, 0.9 ± 0.3 ; diisobutyl ketone, 1.5 ± 0.5 ; trichloroethene, 0.27 ± 0.08 ; tetrachloroethene, 0.13 ± 0.04 . No previous determinations of these rate constants have been found in the literature. Rate constants for an additional nine monoterpene hydrocarbons have been derived from data recently published by Grimsrud, Westberg, and Rasmussen.

Introduction

During the last six years, the major role of the hydroxyl radical (OH) in atmospheric chemistry and photochemical air pollution has been recognized,¹⁻⁷ and kinetic data for the reaction of OH with both organic and inorganic species have increased substantially.⁸ However, there are currently no published rate constant determinations for the reaction of OH with ketones, chloroethenes, or any of the naturally occurring hydrocarbons such as the monoterpenes. Such rate constant data for the reaction of OH with these three classes of compounds would be useful in part because of their increasing importance for modeling the atmospheric processes occurring both in urban and rural atmospheres. Specifically, ketones and chlorinated hydrocarbons are components of commercial solvents.^{9,10} Both tri- and tetrachloroethene have been observed in the troposphere at part per trillion (ppt) concentrations of $<5^{11}$ and 20 ppt,^{11,12} respectively, while methyl ethyl ketone has been observed at concentrations of 1-6 parts per billion (ppb).¹³ Monoterpene hydrocarbons have been shown to be present in the atmosphere with source strengths of millions of tons annually.¹⁴ Thus, Rasmussen^{15,16} and co-workers have estimated that, on an individual basis, such naturally occurring hydrocarbons have ambient concentrations in the low ppb range and are largely responsible for the "blue haze" occurring in certain forested areas.¹⁷

This paper describes an extension of our recent experiments in which an environmental chamber has been employed to obtain relative rate constants for the gas phase reaction of the hydroxyl radical with a series of hydrocarbons.^{18,19} In this case we report data for the reaction of OH with three ketones, two chloroethenes, and three monoterpene hydrocarbons using isobutene as a reference compound.

Experimental Section

The experimental methods and procedures employed have been described in detail elsewhere^{18,19} and are only briefly summarized here. Irradiations of the hydrocarbon- NO_x -air system were carried out in a Pyrex chamber²⁰ of approximately 6400-l. volume equipped with externally mounted

Sylvania 40-BL fluorescent lamps whose spectral distribution has been reported elsewhere²¹ (photon flux at 300 nm is approximately 1% of the photon flux maximum at 360 nm). The light intensity, measured as the rate of NO_2 photolysis in nitrogen,²² k_1 , was approximately 0.4 min^{-1} . All gaseous reactants were injected into pure matrix air²³ in the chamber using 100-ml precision bore syringes. Mixtures of the liquid reactants were injected using micropipettes. During irradiation, the chamber temperature was maintained at 305 ± 2 K.

Alkene, terpene, and ketone concentrations were measured by gas chromatography (GC) with flame ionization detection (FID) using the columns and techniques developed by Stephens and Burleson.^{24,25} The chloroethenes were also monitored with GC(FID) using a 10 ft \times $\frac{1}{8}$ in. stainless steel column packed with 10% Carbowax 600 on C22 Firebrick (100/110 mesh). Ozone²⁶ was monitored by means of ultraviolet absorption (Dasibi Model 1003 analyzer), carbon monoxide by gas chromatography (Beckman 6800 air quality analyzer), and NO - NO_2 - NO_x by the chemiluminescent reaction of NO with ozone (TECO Model 14B).

The initial concentrations of reactants are shown in Table I. In addition to these compounds, ethene (20-28 ppb), ethane (48-61 ppb), acetylene (25-37 ppb), propane (13-15 ppb), and variable concentrations of formaldehyde (16-134 ppb), acetaldehyde (0-7 ppb), and acetone (3-19 ppb) were present. Initial concentrations in these experiments were 1200-2100 ppb C of total nonmethane hydrocarbons, 0.58 ppm of NO_x (with an NO_2/NO_x ratio of 0.05-0.10), 5 ppm of CO, and 2900 ppb of methane, together with water vapor at 50% relative humidity. Replicate experiments were carried out in which this mixture was irradiated for 2-3 h with continuous analysis of inorganic species, analysis of hydrocarbons every 15 min, and analysis of monoterpenes, chloroethenes, and ketones every 30 min.

All data were corrected for losses due to sampling from the chamber by subtraction of the average dilution rate (1.2% per hour) from the observed hydrocarbon disappearance rate. The HC/NO_x and NO/NO_2 ratios were chosen to delay the formation of ozone, and ozone was not detected during the irra-

TABLE I: Rates of Disappearance and Rate Constants^a for Selected Ketones, Chloroethenes, and Monoterpene Hydrocarbons at 1 atm in Air at 305 ± 2 K

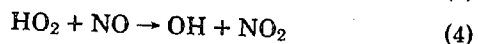
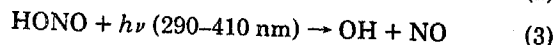
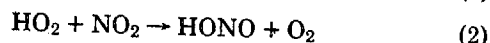
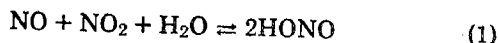
Compound	Initial concn, ppb	Relative rate of disappearance	$k_{OH},^b M^{-1} s^{-1} \times 10^{-10}$
Isobutene	17-20	1.0	3.05 ± 0.31
Propene	5-7	0.49	1.49 ± 0.22
cis-2-Butene	7-8	1.22	3.72 ± 0.56
Methyl ethyl ketone	50-100	0.07	0.20 ± 0.06
Methyl isobutyl ketone	20-70	0.3	0.9 ± 0.3
Diisobutyl ketone	20-32	0.5	1.5 ± 0.5
α -Pinene	10-20	1.14	3.48 ± 0.52
β -Pinene	10-20	1.33	4.06 ± 0.61
d-Limonene	10-20	2.95	9.00 ± 1.35
Trichloroethene	41-161	0.088	0.27 ± 0.08
Tetrachloroethene	14-88	0.044	0.13 ± 0.04

^a Placed on an absolute basis using $3.05 \times 10^{10} M^{-1} s^{-1}$ for OH + isobutene from ref 35. ^b The indicated error limits are $\pm 15\%$, except in the case of the chloroethenes and ketones, for which they are $\pm 30\%$. These represent the estimated overall error limits and include both experimental errors and uncertainties which may occur in assuming that hydrocarbon disappearance is due solely to reaction with OH.

diation period, except in the case of one experiment, for which a small correction for the loss of hydrocarbon due to reaction with ozone was applied to the alkene disappearance rates.

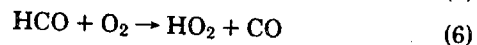
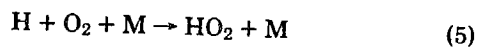
In order to obtain additional data (at lower OH concentrations) to correct for the concurrent photolysis of the ketones as discussed below, irradiations of a mixture of ketones and isobutene were carried out. In these experiments, NO_x , CO, and other hydrocarbons were not added, and, under these conditions, relatively low concentrations of OH ($< 5 \times 10^5$ radicals cm^{-3}) were obtained.

Hydroxyl Radical Source in this System. As discussed previously,¹⁹ the major sources of OH and its precursors in our experimental system are probably the reactions^{4,5,27,28}



The first reaction is now thought to occur slowly homogeneously,²⁹ but its rate is probably significantly faster when the reaction is catalyzed by surfaces. Thus, nitrous acid has been observed in a chamber study of simulated atmospheres carried out in our laboratory,³⁰ while direct evidence for formation of OH radicals in an environmental chamber has been provided recently by Niki, Weinstock, and co-workers.^{31,32}

Reaction 4, of major importance, provides a further source of the OH radical. HO_2 can be formed in air^{33,34} by any mechanism producing H atoms or formyl radicals (e.g., formaldehyde photolysis) via the reactions



Thus any mechanism producing HO_2 in our system is also a means of furnishing OH radicals via reaction 4.

The concentration of OH radicals present during these irradiated HC- NO_x experiments was calculated to be (1.4-3.5)

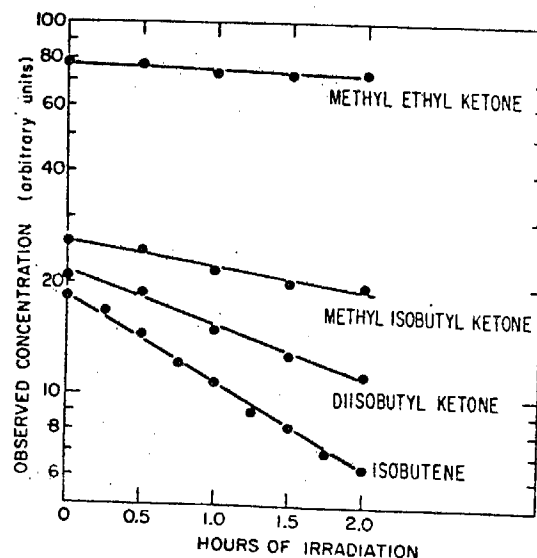


Figure 1. Concentrations of ketones (plotted on a logarithmic scale) during 2-h photolysis of HC- NO_x mixture in air at 305 ± 2 K and 1 atm.

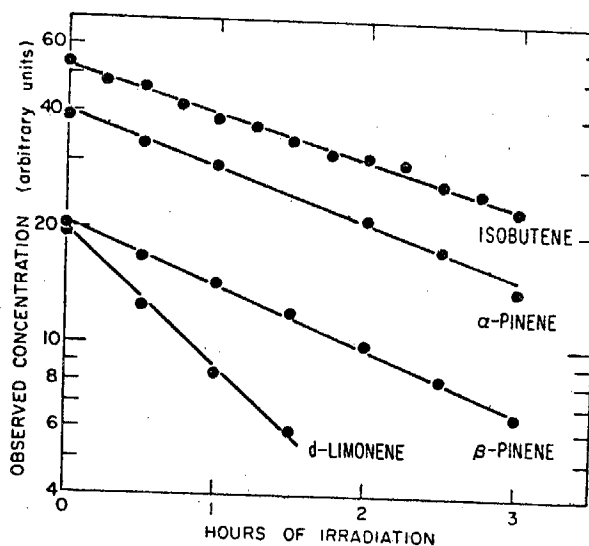


Figure 2. Concentrations of monoterpene hydrocarbons (plotted on a logarithmic scale) during 3-h photolysis of HC- NO_x mixture in air at 305 ± 2 K and 1 atm.

$\times 10^6$ radicals cm^{-3} using the observed rates of isobutene disappearance (corrected for dilution) and the previously determined rate constant for OH + isobutene.³⁵ These concentrations are of the same order as those observed directly in ambient air.^{31,32,36,37}

Results and Discussion

Typical rates of disappearance observed during a 2-h irradiation of the three ketones and 3-h irradiations of the three monoterpene hydrocarbons and the two chloroethenes are shown in Figures 1, 2, and 3, respectively. Isobutene was used as the reference compound (and is included in each figure), rather than *n*-butane which was used in our previous studies,^{18,19} because its reactivity was closer to that of the terpenes, and its rate of decay could be measured more accurately in our system. In addition, the ratio of k_{OH}/k_{O_3} for isobutene is greater^{32,35} than that for any of the other olefins studied, thus minimizing any contribution to the disappearance rate due to reaction with ozone. Table I gives the disappearance rates

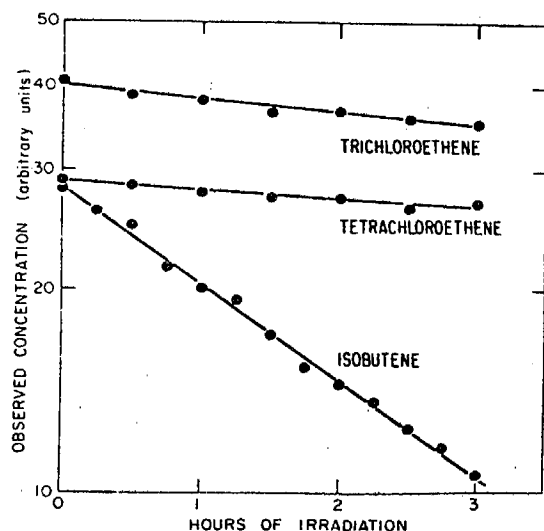


Figure 3. Concentrations of chloroethenes (plotted on a logarithmic scale) during 3-h photolysis of HC-NO_x mixture in air at 305 ± 2 K and 1 atm.

(corrected for dilution) for these reactants relative to that for isobutene based on data for the three separate experiments for monoterpenes and four separate experiments for methyl isobutyl and diisobutyl ketone and chloroethenes. Methyl ethyl ketone was present in all experiments.

Employing the fact that a range of OH concentrations (2.0×10^5 – 3.5×10^6 radicals cm⁻³) was observed in these experiments, corrections to the measured rates of disappearance of the ketones were made for the possible small contribution from photolysis of these compounds. These corrections were made in the following manner. The observed rate of disappearance of a ketone is given by

$$d \ln [\text{ketone}]/dt = k_K[\text{OH}] + k_{hv} \quad (7)$$

where k_K and k_{hv} are the rate constants for reaction with OH and photolysis, respectively. The isobutene disappearance rate is controlled solely by reaction with OH, hence

$$[\text{OH}] = \frac{d \ln [\text{isobutene}]}{dt k_{iB}} \quad (8)$$

where k_{iB} is the rate constant for reaction of OH with isobutene. Thus, substituting for [OH] in eq 7

$$\frac{d \ln [\text{ketone}]}{dt} = \frac{k_K}{k_{iB}} \frac{d \ln [\text{isobutene}]}{dt} + k_{hv} \quad (9)$$

Based on eq 9, the relative rates of ketone disappearance were determined from the slopes of plots of $d \ln [\text{ketone}]/dt$ vs. $d \ln [\text{isobutene}]/dt$. The intercepts of these plots gave the rate constants for photolysis. For methyl ethyl, methyl isobutyl, and diisobutyl ketone the ratios k_K/k_{iB} were 0.07, 0.3, and 0.5, respectively, and the photolysis rate constants, k_{hv} , were 0.007, 0.014, and 0.25 h⁻¹, respectively.

On the basis that the OH radical is the species dominantly responsible for the hydrocarbon depletion during the 2- or 3-h irradiations (as discussed in detail in our earlier papers),^{18,19} absolute rate constants were derived from the relative rates of disappearance using Atkinson and Pitts³⁵ value of $(3.05 \pm 0.31) \times 10^{10}$ M⁻¹ s⁻¹ for the reaction of OH with isobutene. These results are shown in Table I. It should be noted that the ratio of rate constants (0.5 and 1.2, respectively) obtained here for propene and *cis*-2-butene relative to isobutene are in excellent agreement with the ratios obtained by Atkinson and Pitts (0.5 and 1.1, respectively).³⁵

Ketones. To our knowledge, the data presented here represent the first experimental determination of rate constants for the reaction of the OH radical with any ketones in the gas phase. The only literature value for ketones is an estimated rate constant of 2.1×10^9 M⁻¹ s⁻¹ for the reaction of OH with methyl ethyl ketone, which was made by Demerjian, Kerr, and Calvert⁵ on a thermochemical basis. This value is in remarkably good agreement with the experimental value obtained here (2.0×10^9 M⁻¹ s⁻¹).

The rate constants for the reaction of OH with the two other ketones reported here are significantly larger than that for methyl ethyl ketone. Thus, the rate constant for diisobutyl ketone is about the same as that for OH + propene.^{8,19,35} The dominant mode of reaction of OH with ketones is expected to be one of hydrogen abstraction. This is consistent with the increased rate constant in going from methyl ethyl ketone to diisobutyl ketone reflecting a weaker C–H bond strength in going to more highly substituted ketone.

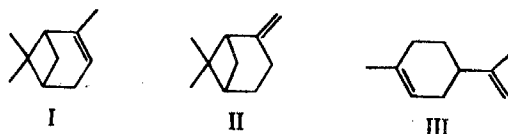
Acetone is relatively stable under conditions employed in our photooxidation studies, and, consequently, the rate constant for OH + acetone was not measured. Based on the fact that the C–H bond strength in acetone (98 kcal) is 6 kcal stronger than that for methyl ethyl ketone (92 kcal), one would expect OH to react significantly slower with acetone than with methyl ethyl ketone.

Chloroethenes. Rate constants for the gas phase reactions of OH with tri- and tetrachloroethene (C₂HCl₃ and C₂Cl₄, respectively) have not been reported previously. The rate constants found in this study are 0.5 and 0.25, respectively, of the rate constant for OH + C₂H₄.¹⁹ This difference in reactivity for the chloro-substituted ethenes and ethene is consistent with the results of Sanhueza and Heicklen,^{38–40} who reported that the rates of reaction of O(³P) with C₂HCl₃ and C₂Cl₄ were the same and were both a factor of 10 less than that for the reaction of O(³P) with ethene.

Our results show that trichloroethene is more reactive with respect to attack by OH than tetrachloroethene. This is in agreement with the results of Lissi⁴¹ for CH₃O reactions and Franklin et al.⁴² for Cl atom reactions with these compounds. These workers found relative rates for attack on C₂HCl₃ and C₂Cl₄ of 2.2 and 2.6 for CH₃O and Cl, respectively, compared to 2.0 for OH, as found in the present study. Gay et al.⁴³ recently reported results from a photooxidation study of chloroethenes which, while not directly comparable to the present study due to the presence of substantial concentrations of ozone, showed that C₂HCl₃ disappeared more rapidly than C₂Cl₄ (near the beginning of their irradiations, when ozone concentrations were relatively low, the ratio of the rates of disappearance was ~2).

Since addition is likely to be the primary reaction pathway for attack by OH, the relative reactivity of C₂H₄, C₂HCl₃, and C₂Cl₄ should reflect the relative magnitudes of the ionization potentials of these molecules, which are 10.66, 9.48, and 9.34 eV, respectively. Our results are consistent with this trend.

Monoterpene Hydrocarbons. The terpenes experimentally investigated were α-pinene (I), β-pinene (II), and *d*-limonene (III). The detection limit for ozone in these experiments was



~1 ppb, and, since no ozone was detected during irradiations of the terpenes, an upper limit to the contribution due to reaction with ozone to the observed rates of terpene disap-

TABLE II: Reactivity of Selected Monoterpenes with O(³P), O₃, and OH

Compound	Rate constant, M ⁻¹ s ⁻¹		
	O(³ P) ^a	O ₃	OH ^e
α-Pinene	1.60 ± 0.06 × 10 ¹⁰	2.0 × 10 ⁵ , ^b 1.0 × 10 ^{5c} 8.8 × 10 ^{4d}	3.5 × 10 ¹⁰
β-Pinene	1.51 ± 0.06 × 10 ¹⁰	2.2 × 10 ^{4d}	4.1 × 10 ¹⁰
<i>d</i> -Limonene	6.50 ± 0.52 × 10 ¹⁰	3.9 × 10 ^{5d}	9.0 × 10 ¹⁰

^a Reference 49. ^b Reference 48. ^c Reference 45. ^d Reference 16. ^e This work.

pearance can be calculated. Thus, assuming an ozone concentration of ≤1.0 ppb, and using published rate constants for the reaction of ozone with the terpenes,^{16,43-45} an upper limit of 7% of the overall disappearance rate is obtained for the case of *d*-limonene (the worst case) at the lowest OH concentration present in these experiments (1.4 × 10⁶ radicals cm⁻³).

It is interesting to note that the rate constant, 3.7 × 10¹⁰ M⁻¹ s⁻¹, obtained in this study for OH + *cis*-2-butene, a component in the hydrocarbon mix (Table I) used in this set of experiments, is in good agreement with the values of 3.2 × 10¹⁰ and 3.7 × 10¹⁰ M⁻¹ s⁻¹, obtained by Atkinson and Pitts³⁵ and Morris and Niki,⁴⁶ respectively, although our value is somewhat higher than the value of 2.6 × 10¹⁰ M⁻¹ s⁻¹ obtained by Fischer et al.,⁴⁷ in these three studies, the rate constant was determined from elementary reaction measurements.

Table I shows the absolute rate constant values obtained for the terpenes. Clearly, these natural hydrocarbons react very rapidly with OH. For example, α-pinene reacts about 3 × 10⁵ times faster with OH than with ozone.^{16,48} Thus, for an ozone concentration of 3 × 10¹² molecules cm⁻³ (0.12 ppm) and an OH concentration of 10⁷ radicals cm⁻³, the rates of disappearance of α-pinene due to reaction with O₃ and OH, respectively, will be essentially equal. A comparison of the rates of the three terpenes with O(³P), O₃, and OH is given in Table II.^{16,45,46} Within the experimental errors for the rate constants for OH + α- and β-pinene, the trend observed for reaction with OH is the same as that observed for reaction with O(³P) and O₃.

Grimsrud, Westberg, and Rasmussen (GWR)¹⁶ have reported the relative rates of photooxidation of a series of monoterpene hydrocarbons using mixtures of 10 ppb of the monoterpene and 7 ppb of nitric oxide, which were irradiated for periods ranging between 60 and 120 min. Making the reasonable assumption that, as in the case of our studies, OH is the major species depleting the hydrocarbon in their experiments, then a series of rate constants relative to isobutene (which was included in the GWR study) can be generated in the same manner as described above. The data from GWR are given in Table III relative to isobutene = 1.0.

Considering the uncertainties involved in this approach (including a lack of knowledge of the exact ozone concentrations formed in the experiments of GWR), the agreement between our results for the reaction of OH with α- and β-pinene and *d*-limonene and those shown in the fourth column of Table III is quite good and, except in the case of α-pinene, well within the estimated experimental uncertainty for our determinations. The fact that our value of OH + *d*-limonene is only slightly higher than GWR suggests that little or no O₃ was formed in their experiments, since there was less than 1 ppb formed during our irradiations.

TABLE III: Relative Reaction Rates of Monoterpene Hydrocarbons and Rate Constants^a for Their Reaction with the OH Radical Based on Data from Grimsrud, Westberg, and Rasmussen (Ref 16)

Hydrocarbon	Structure	Rel reactivity	k _{OH} , M ⁻¹ s ⁻¹ × 10 ⁻¹⁰
<i>p</i> -Menthane		0.13	0.40
<i>p</i> -Cymene		0.30	0.92 (0.78 ± 0.16) ^b
Isobutene		1.0	3.05
β-Pinene		1.3	4.0 (4.1 ± 0.6) ^c
Isoprene		1.5 _s	4.7 (4.6 ± 0.9) ^d
α-Pinene		1.5 _s	4.7 (3.5 ± 0.5) ^c
3-Carene		1.7	5.2
β-Phellandrene		2.3	7.0
Carvomenthene		2.5	7.6
<i>d</i> -Limonene		2.9	8.8 (9.0 ± 1.4) ^c
Dihydromyrcene		3.6	10.1
Myrcene		4.5	13.7
<i>cis</i> -Ocimene		6.3	19.2

^a Placed on an absolute basis using 3.05 × 10¹⁰ M⁻¹ s⁻¹ for OH + isobutene from ref 35. ^b For *p*-ethyltoluene which is structurally similar (ref 19). ^c Present work (see Table II). ^d For 1,3-butadiene which is structurally similar (ref 19).

A further check on the validity of using the results of Grimsrud, Westberg, and Rasmussen¹⁶ to obtain OH rate constant data is provided by the values derived for the reaction of OH with *p*-cymene and isoprene. *p*-Cymene is structurally very similar to *p*-ethyltoluene, and hence the OH rate constants for these two compounds should be comparable. In fact, this is the case with the value for OH + *p*-cymene of 9.1 × 10⁹ M⁻¹ s⁻¹ derived from the data of GWR being very close to that obtained for OH + *p*-ethyltoluene, 7.8 × 10⁹ M⁻¹ s⁻¹, in our previous study.¹⁹ Likewise, isoprene is structurally similar to 1,3-butadiene, and the rate constant derived for isoprene of 4.7 × 10¹⁰ M⁻¹ s⁻¹ is consistent with that previously measured¹⁹ for OH + 1,3-butadiene of 4.6 × 10¹⁰ M⁻¹ s⁻¹. On the basis of these comparisons, it appears valid to use the photooxidation data of Grimsrud, Westberg, and Rasmussen¹⁶ to obtain OH rate constant data for the series of monoterpenes which they investigated.

Conclusion

Relative rate constants have been experimentally determined for the reaction of OH with eight compounds, and these rate constants have been placed on an absolute basis using the literature value for the rate constant for OH + isobutene.³⁵ In the same manner, rate constants for the reaction of OH with nine additional compounds (monoterpene hydrocarbons) for

which no previous rate constants are available have been derived from data recently published by Grimsrud, Westberg, and Rasmussen.¹⁶

The comparatively large rate constants obtained for the ketones and monoterpene hydrocarbons indicate that they will be quite reactive in the troposphere. The implications for photochemical oxidant control strategies of the chemical reactivity of the ketones, chloroethenes, and terpenes are discussed in detail elsewhere.^{50,51}

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Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical

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■ By use of relative and absolute rate constants for the reaction of the hydroxyl radical (OH) with a number of alkanes, alkenes, aromatics, and ketones, a reactivity scale is formulated based on the rate of removal of hydrocarbons and oxygenates by reaction with OH. In this five-class scale, each class spans an order of magnitude in reactivity relative to methane. Thus, assigned reactivities range from <10 for Class I (containing only methane) to $>10^4$ for Class V containing the most reactive compounds (e.g., *d*-limonene). This scale differs in several significant ways from those presently utilized by air pollution control agencies and various industrial laboratories. For example, in contrast to other scales based on secondary manifestations such as yields of ozone and eye irritation, it focuses directly on initial rates of photooxidation. The proposed scale also provides a clearer understanding of the importance of alkanes in the generation of ozone during periods of prolonged irradiation. The present scale can be readily extended to include additional organic compounds (e.g., natural and anthropogenic hydrocarbons, oxygenates, chlorinated solvents), once their rate of reaction with OH is known.

It has been recognized for many years (1-21) that all hydrocarbons occurring in polluted atmospheres are not equally effective in producing photochemical oxidant, and hence that the application of cost effective strategies for the control of hydrocarbons requires that more stringent emissions reductions be applied to the more reactive organic compounds (22-25). This in turn has led to a continuing requirement for a rational assessment of hydrocarbon reactivity as a basis for control decisions. Such an assessment is particularly critical since attainment of the Federal air quality standard for photochemical oxidant has been sought largely through the stringent control of hydrocarbon emissions (26-27).

The first effort to formulate and apply a practical hydrocarbon reactivity scale was taken in 1966 with the implementation by the Los Angeles Air Pollution Control District (LAAPCD) of a regulation, known as Rule 66, to limit solvent organic emissions on the basis of their capacity for promoting photochemical smog formation (24-25). This rule and other conceptions of reactivity scales (28) represented a major advance in the application of the information then available concerning the mechanisms of photochemical smog formation to the development of practical air pollutant emission control strategies.

Not surprisingly however, both in the past and present, there have been significant differences in hydrocarbon reactivity scales proposed by local, regional, and national air pollution control agencies (23, 29-31) as well as by industry (14, 16). As shown in Table I, this can lead to very large differences in emission inventory estimates and in approaches to hydrocarbon control (29, 32, 33). In this case, reactive hydrocarbon emission inventory levels calculated by Goeller et al. (32) using hydrocarbon reactivity definitions of the Environmental Protection Agency (EPA) on the one hand, and the California Air Resources Board (ARB) and LAAPCD on the other, differed by factors of 3 to 4!

A second problem common to virtually all previous reactivity classifications has been their reliance on smog chamber data obtained for relatively short irradiation (~ 2 -6 h) periods.

Thus, the recent concern over oxidant formation resulting from longer irradiations during pollutant transport to regions downwind of urban sources introduces additional difficulties both in defining what constitutes a reactive hydrocarbon and in categorizing degrees of reactivity. For example, a compound such as propane, the major component in liquefied petroleum gas (LPG) and often cited as a "clean" fuel, is now known (34-36) to contribute to the formation of photochemical oxidants in the later stages of day-long irradiation periods. However, on the basis of data obtained during short-term irradiations, propane has been classified as "unreactive" in a reactivity scale proposed (23) by B. Dimitriades of the EPA (hereafter referred to as the EPA reactivity scale).

Altshuller and Bufalini (9, 17) have reviewed the various definitions of hydrocarbon reactivity and summarized results of numerous studies up to 1970. The criteria used for evaluating hydrocarbon reactivity include hydrocarbon consumption, the conversion of nitric oxide to nitrogen dioxide, ozone formation, aerosol formation, eye irritation, and plant damage. It is generally agreed that the criteria most suitable with respect to photochemical oxidant control strategies are ozone dosage or maximum ozone concentration (29). However, establishing a definitive hydrocarbon reactivity scale to be applied specifically to the control of ozone formation requires an extensive and lengthy experimental program in which the ozone-forming capability of each individual hydrocarbon is determined under simulated atmospheric conditions, including long-term irradiation (i.e., 12-14 h).

An alternative basis for assessing hydrocarbon reactivity, which would appear to have considerable utility and a valid experimental foundation, is the formulation of a reactivity scale based on the rate of disappearance of hydrocarbons due to reaction with the hydroxyl radical, the key intermediate species in photochemical air pollution.

Results and Discussion

It is only in the last six years that the critical role of OH in photochemical smog formation has been generally recognized (37-40) and that appreciable rate constant data have become available for the reaction of OH with several classes of hydrocarbons. The importance of OH as a reactive intermediate relative to species such as O_3 , $O(^3P)$, and HO_2 has been shown previously (39-41) through computer modeling of smog chamber data. For example, Niki et al. (39) showed that the reactivity of a number of hydrocarbons, as measured by the rate of conversion of NO to NO_2 , correlated significantly better with OH rate constants than with either $O(^3P)$ or O_3 rate constants.

Table I. Comparison of Reactive Hydrocarbon Inventory Levels for Fixed Sources Under Alternative Reactivity Assumptions (from Ref. 32 Based on Pre-1973 Data)

Control strategy	Reactive hydrocarbons, tons/day		
	Consistent EPA	ARB-LAAPCD	Rand Corp.
1970	876.0	228.3	636.3
1975 nominal	427.3	102.2	239.9
1975 maximal	290.6	57.7	129.9

The utility of a large environmental chamber in obtaining relative rate constants with an accuracy of $\pm 20\%$ for the reaction of the hydroxyl radical with a variety of hydrocarbons was demonstrated in an earlier study in this laboratory (41). This method has recently been extended to an investigation of more than a dozen additional hydrocarbons, including seven compounds for which OH rate constants are not currently available. The detailed kinetic data derived from this investigation have been reported elsewhere (42). In these studies we determined the relative rates of disappearance of selected alkanes, alkenes, and aromatic hydrocarbons under simulated atmospheric conditions of temperature, pressure, concentrations, light intensity, and other trace contaminants (NO_x , CO, hydrocarbons, water). These relative rate constants were placed on an absolute basis using the published rate constants for OH + *n*-butane. The assumption that OH was responsible for the hydrocarbon disappearance under the experimental conditions employed (41) was subsequently supported by the very good agreement between OH rate constants determined for the individual compounds using flash photolysis-resonance fluorescence techniques (43, 44) and those obtained in the initial chamber study (41). The general validity of the chamber method for obtaining OH rate constants is illustrated in Figure 1 where the good correspondence between chamber values (41, 42) and the available literature values [(45) and references in Table IV] is shown graphically.

The importance of the chamber method for the purposes of formulating a reactivity scale is the simultaneous determination of valid rate constants for reactions of OH with a large number and wide variety of atmospherically important hydrocarbons. This substantially expands the number of compounds which can be incorporated, now and in the near future, in the resulting reactivity scale. In this regard we are currently extending (46) the chamber method to the determination of rate constants for reactions of OH with natural hydrocarbons, such as terpenes, and solvent hydrocarbons, such as ketones and chloroethenes, for which no data currently exist. Preliminary kinetic data (46) for selected natural hydrocarbons and ketones are included in our proposed reactivity scale.

Use of OH Rate Constants as a Reactivity Index. From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in our chamber simulations, we conclude that, to a good approximation, this

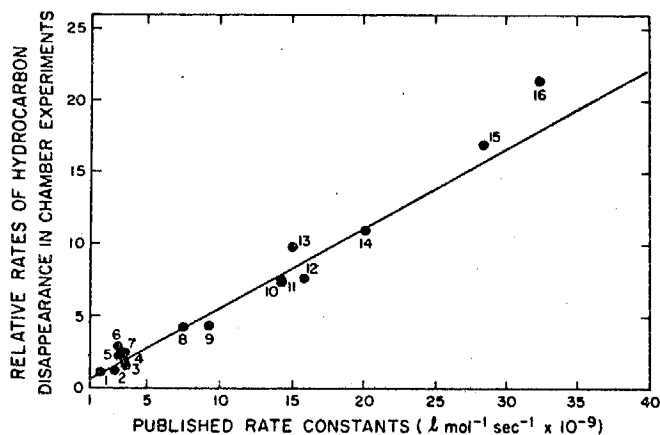


Figure 1. Comparison of relative rates of hydrocarbon disappearance determined by environmental chamber method (refs. 41 and 42) with selected published rate constants (cited in Table IV) for reaction of those hydrocarbons with OH radicals

Line shown represents one to one correspondence and has slope of $(1/1.8) \times 10^{-9} \text{ mol s l}^{-1}$. Compounds shown are: 1, *n*-butane; 2, isopentane; 3, toluene; 4, 2-methylpentane; 5, *n*-hexane; 6, ethene; 7, 3-methylpentane; 8, *p*-xylene; 9, *o*-xylene; 10–11, *m*-xylene; 12, 1,2,3-trimethylbenzene; 13, propene; 14, 1,2,4-trimethylbenzene; 15, 1,3,5-trimethylbenzene; 16, *cis*-2-butene

Table II. Effect of 0.1 PPM Ozone on Calculated Lifetimes of Selected Alkenes Based on Reaction with OH Radicals ($1 \times 10^7 \text{ Radicals/cm}^3$)^a at 300 K

Alkene	OH rate constants, ^b $\text{l. mol}^{-1} \text{ s}^{-1}$	Half-life ^c for $[\text{O}_3] = 0, \text{ h}$	Half-life ^d for $[\text{O}_3] = 0.1 \text{ ppm, h}$
Ethene	3.8×10^9	3.0	2.8
Propene	1.5×10^{10}	0.76	0.67
<i>cis</i> -2-Butene	3.2×10^{10}	0.36	0.20
1,3-Butadiene	4.6×10^{10}	0.25	0.24

^a Concentration used in these calculations—see text. ^b See references in Table IV. ^c $t_{1/2} = 0.693/k_{\text{OH}}[\text{OH}]$ under the assumption of attack only by OH. ^d $t_{1/2} = 0.693/(k_{\text{OH}}[\text{OH}] + k_{\text{O}_3}[\text{O}_3])$; k_{O_3} taken from refs. 45 and 59.

correlation can be extrapolated to the atmosphere for alkenes in ambient air parcels during the early morning hours when ozone levels are generally quite low ($\leq 0.05 \text{ ppm}$), and for alkanes and aromatics at essentially all times and locations. The latter assumption, namely, that an OH rate constant is a good "reactivity index" for alkanes and aromatics throughout an irradiation day (or multiple irradiation days), rests upon the fact that the rates of reaction of these classes of hydrocarbons with species such as ozone, $\text{O}(^3\text{P})$ atoms, and hydroperoxyl radicals are several orders of magnitude slower than with OH (45, 47–49). For example, even at the highest ozone concentrations experienced in ambient atmospheres, O_3 will not contribute significantly to the photooxidation of alkanes and aromatics.

This is in contrast to the case for alkenes which, although the rate constants for reaction of O_3 with alkenes are not particularly large (45), react rapidly with ozone at the average concentrations commonly encountered in polluted ambient air (~ 0.1 – 0.2 ppm). The approximate magnitude of the effect of ozone on the atmospheric lifetimes of alkenes is given in Table II. From their OH rate constants (see Table IV), atmospheric lifetimes for four alkenes were obtained by assuming an OH radical concentration in polluted atmospheres of $10^7 \text{ radicals cm}^{-3}$, which is a reasonable value on the basis of both model calculations (50) and recent atmospheric measurements (51–53). The half-life given in column 3 of Table II is defined as $t_{1/2} = 0.693/k(\text{OH})$, and assumes depletion of the hydrocarbon solely by the hydroxyl radical. When one assumes an average concentration of 0.10 ppm of O_3 , the more reactive alkenes show considerably shorter half-lives (column 4). For example, the lifetime of *cis*-2-butene in the atmosphere is 0.36 h assuming only reaction with OH, but this is reduced to 0.20 h when reaction with O_3 at a concentration of 0.1 ppm is considered.

Proposed Reactivity Scale. Under the assumption that hydrocarbon depletion is due solely to attack by OH (with the qualification noted for alkenes), we propose a five-class reactivity scale based on hydrocarbon disappearance rates due to reaction with OH. The ranges of reactivities for the five proposed classes each span an order of magnitude in reactivity relative to methane and are shown in Table III. The hydrocarbon half-lives, as defined above, are also shown for each reactivity range.

Hydroxyl radical rate constant data for a wide range of atmospheric hydrocarbons have been taken from the literature as well as from our own studies and are compiled and referenced in Table IV. The assignment of these compounds in the various classes of our proposed reactivity scale is shown in the last column of Table IV. For interest, carbon monoxide is included in this table since, although it is not a hydrocarbon, it is present in polluted urban atmospheres but is generally regarded as being "unreactive" in ambient air. Thus, carbon

monoxide appears as being somewhat reactive in Class II, which also includes ethane and acetylene. In our current compilation of compounds, methane is the only compound listed which appears in Class I, and 2-methyl- and 2,3-dimethyl-2-butene and *d*-limonene are the only compounds in Class V. Several of the higher alkenes and 1,3-butadiene appear at the upper end of Class IV. Data from our recent study of monoterpene hydrocarbons (46) indicate that many of these compounds will appear in Class V (54).

Comparison with Other Scales. The ranking of reactivities for the aromatic hydrocarbons in our scale is essentially the same as that obtained by Altshuller et al. (4) and by Kopczynski (7, 17). Although our proposed scale is based solely on hydrocarbon disappearance rates, Altshuller and Bufalini (17) have shown that this measure of reactivity is very similar to the one based on nitric oxide oxidation rates. They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and

Cohen (6) and Glasson and Tuesday (8) was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle (1), Stephens and Scott (3), and Tuesday (5). We are currently investigating methods of quantitatively relating hydrocarbon consumption to nitric oxide oxidation and ozone formation, the parameter of greatest interest in formulating control strategies for oxidant reduction.

As indicated above, Rule 66 formulated by the LAAPCD in 1966 represented the first hydrocarbon control measure based on photochemical reactivity. Although this regulation has been effective, results from recent studies (34-36) indicate that the 4-6 h irradiations (25), from which assignments of the degree of reactivity of hydrocarbons were made in formulating Rule 66, did not give sufficient recognition to the ozone-forming potential of slow reactors such as *n*-butane and propane. Consequently, it is now realized that measures more stringent than Rule 66 are necessary to achieve reductions in ozone formation to levels approaching those mandated by the U.S. Clean Air Act Amendments of 1970.

Recognition of such deficiencies in current hydrocarbon control regulations has led to reexamination of present hydrocarbon reactivity classifications. The focus of these re-evaluations has been the five-class reactivity scale (see Table V) proposed by B. Dimitriadis at the EPA Solvent Reactivity Conference in 1974 (23). Significant changes have been suggested for this reactivity classification by the California ARB (29, 30), the LAAPCD (31), the EPA (55), and by industry. However, since no final conclusions have been reached by any of these agencies at this time, we will restrict comparison of our proposed scale to the 1974 EPA scale.

Table III. Reactivity Scale for Hydrocarbons Based on Rate of Disappearance of Hydrocarbon Due to Reaction with Hydroxyl Radicals

Class	Half-life ^a	Reactivity rel to methane (=1)
I	>9.9 days	<10
II	24 h to 9.9 days	10-100
III	2.4-24 h	100-1000
IV	0.24-2.4 h	1000-10 000
V	<0.24 h	>10 000

$$^a t_{1/2} = 0.693/k_{OH}[OH].$$

Table IV. Proposed Reactivity Classification of Hydrocarbons and CO Based on Reaction with Hydroxyl Radicals

Compound	$k_{OH} + \text{Cpd (l. mol}^{-1} \text{ s}^{-1}) \times 10^{-9}$	Ref. ^a	Reactivity rel to methane	Proposed class, see Table III
Methane	0.0048	(60)	1	I
CO	0.084	(45)	18	II
Acetylene	0.11	(45, 61, 66)	23	II
Ethane	0.16	(62)	33	II
Benzene	0.85	(43, 44)	180	III
Propane	1.3	(63)	270	III
<i>n</i> -Butane	1.8	(41, 42)	375	III
Isopentane	2.0	(42)	420	III
Methyl ethyl ketone	2.1	(46)	440	III
2-Methylpentane	3.2	(42)	670	III
Toluene	3.6	(43, 44)	750	III
<i>n</i> -Propylbenzene	3.7	(42)	770	III
Isopropylbenzene	3.7	(42)	770	III
Ethene	3.8	(42, 64-66)	790	III
<i>n</i> -Hexane	3.8	(42)	790	III
3-Methylpentane	4.3	(42)	900	III
Ethylbenzene	4.8	(42)	1000	III-IV
<i>p</i> -Xylene	7.45	(41, 43)	1530	IV
<i>p</i> -Ethyltoluene	7.8	(42)	1625	IV
<i>o</i> -Ethyltoluene	8.2	(42)	1710	IV
<i>o</i> -Xylene	8.4	(41, 43)	1750	IV
Methyl isobutyl ketone	9.2	(46)	1920	IV
<i>m</i> -Ethyltoluene	11.7	(42)	2420	IV
<i>m</i> -Xylene	14.1	(41, 43)	2920	IV
1,2,3-Trimethylbenzene	14.9	(41, 43)	3100	IV
Propene	15.1	(67)	3150	IV
1,2,4-Trimethylbenzene	20	(41, 43)	4170	IV
1,3,5-Trimethylbenzene	29.7	(41, 43)	6190	IV
<i>cis</i> -2-Butene	32.3	(67)	6730	IV
β -Pinene	42	(46)	8750	IV
1,3-Butadiene	46.4	(42)	9670	IV-V
2-Methyl-2-butene	48	(68)	10 000	V
2,3-Dimethyl-2-butene	67	(69)	14 000	V
<i>d</i> -Limonene	90	(46)	18 800	V

^a Where more than one reference is cited, an average value is given for the rate constant.

Table V. Proposed EPA Reactivity Classification of Organics (from Ref. 23, 1974)

Class I, nonreactive	Class II, reactive	Class III, reactive	Class IV, reactive	Class V, reactive
C ₁ -C ₃ paraffins	Mono-tertiary- alkyl benzenes	C ₄ + paraffins	Primary and secondary alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	α -Methyl styrene
Benzene	Tertiary-alkyl acetates	Styrene	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	<i>n</i> -Alkyl ketones	Primary and secondary alkyl acetates	Tri- and tetra-alkyl benzenes
Acetone		<i>N</i> -methyl pyrrolidone	Primary and secondary alkyl alcohols	Unsaturated ketones
Methanol		<i>N,N</i> -dimethyl acetamide	Cellosolve acetate	Diacetone alcohol
Tertiary-alkyl alcohols		Partially halogenated paraffins	Partially halogenated olefins	Ethers
Phenyl acetate		Partially halogenated paraffins		Cellosolves
Methyl benzoate				
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons				
Reactivity rating: 1.0	3.5	6.5	9.7	14.3

Briefly, the EPA has proposed, on the basis of previous experimental studies, that methane, ethane, acetylene, propane, and benzene are essentially nonreactive for typical urban ambient hydrocarbon-NO_x ratios (23) and these compounds are placed in Class I on their scale. Three other classes have been proposed for mobile source hydrocarbon emissions (56)—Class III (C₄ and higher alkanes), Class IV (aromatics less benzene), and Class V (alkenes). When stationary source hydrocarbons, including solvents (Class II), are added to the list, five classes are suggested as shown in Table V.

The reactivity classification proposed here (Tables III and IV) can be compared with that suggested by the EPA (Table V). It is evident that several significant differences emerge:

- The C₁-C₃ alkanes are given equal weighting in the EPA scale, and all are designated unreactive, whereas our scale clearly differentiates among the three compounds from methane in Class I and ethane in Class II to the more reactive propane in Class III.
- According to our proposed classification, benzene and *n*-butane are of similar reactivity, whereas the EPA scale places them in Class I and III, respectively.
- All the alkenes are placed in Class V of the EPA scale, whereas our proposed scale shows a differentiation in reactivity from ethene in Class III to 2,3-dimethyl-2-butene in Class V.
- Our scale gives recognition to the high reactivity of natural hydrocarbons such as β -pinene and *d*-limonene, placing these in Class IV and V, respectively. The present published EPA scale does not give a classification for natural hydrocarbons, although they could be loosely categorized as substituted alkenes in Class V.

In addition to noting these differences, some similarities exist between the two scales. For example, our scale shows that 1,3-butadiene is highly reactive which is consistent with previous studies indicating it to be a facile precursor of eye irritants (17) and highly effective in producing oxidant during irradiation of HC-NO_x mixtures (57). Also, methanol would appear in the low half of Class II in our scale based on a recent determination of the rate constant for OH attack on methanol (58). The value found was $k(\text{OH}+\text{CH}_3\text{OH})/k(\text{OH}+\text{CO}) = 0.63$ at 298 K. This reduces to $5.3 \times 10^7 \text{ l. mol}^{-1} \text{ s}^{-1}$ based on $k(\text{OH}+\text{CO}) = 8.4 \times 10^7 \text{ l. mol}^{-1} \text{ s}^{-1}$ (45). Hence, both our scale and the EPA's show methanol to be relatively unreactive.

It should be emphasized that the classification proposed in our scale is not strictly applicable to compounds which

undergo significant photodissociation in the atmosphere, for example, aliphatic aldehydes. In such cases, the compound will be more reactive than predicted from a scale based on hydrocarbon depletion due solely to OH attack. However, our proposed classification emphasizes that most compounds react in polluted atmospheres and suggests that the Class I scale be reserved only for the few compounds which have half-lives greater than about 10 days.

Conclusion

Our proposed reactivity scale based on the depletion of hydrocarbons by reaction with the OH radical has utility in assessing hydrocarbon chemical behavior in polluted ambient air. Since only those organic compounds which participate in atmospheric reactions are of consequence in the chemical transformations in ambient air, their relative reactivity toward OH is a useful and directly measurable index of their potential importance in the production of secondary pollutants.

One advantage of the proposed scale is that, because it is based on the individual rate constants for hydrocarbon reaction with OH, any degree of gradation in reactivity may be used to formulate any desired number of classes—from relatively few to a large number of classes or even an ordered ranking of compounds. A second strength of the present scale is that it can be readily extended to include additional organic compounds once their rate of reaction with OH is known. Finally, the proposed scale gives greater weight than previous reactivity scales to the alkanes and a number of aromatic hydrocarbons, which require a longer period of time to react but can contribute significantly to ozone formation during longer irradiation periods, e.g., during their transport downwind from urban centers—a phenomenon of increasing concern to air pollution control agencies.

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DEVELOPMENT AND APPLICATION OF A HYDROCARBON REACTIVITY SCALE
BASED ON REACTION WITH THE HYDROXYL RADICAL

by

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Abstract

Measurements of the relative rate constants for the reaction of the hydroxyl radical (OH) with some 35 atmospherically important hydrocarbons have been made in the SAPRC 6400 & glass irradiation chamber. These rate constants were placed on an absolute basis using literature values for either n-butane or isobutene and have been augmented with OH rate data obtained by elementary reaction measurements and other appropriate data, such as that from photo-oxidation studies, from which relative and absolute OH rate constants could be calculated.

Utilizing these data, a reactivity scale for some 80 compounds, including alkenes, alkanes, aromatics, oxygenates, and naturally occurring hydrocarbons, has been formulated based on the removal of the hydrocarbons by reaction with OH. The resulting scale is an ordering of the reactivities of the hydrocarbons relative to methane. The scale can be divided into an arbitrary number of classes for purposes of application to control strategies or comparison with other reactivity scales.

Some comparisons of the present scale with proposed EPA and ARB reactivity scales are made, and the implications of the present scale for the role of alkanes and a number of aromatic hydrocarbons in the formation of ozone in regions downwind of urban centers is analyzed.

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Introduction

A major result of the photooxidation studies of the past 20 years¹⁻²⁶ has been the recognition that atmospherically important hydrocarbons do not all contribute equally to the production of photochemical oxidant, and hence that the application of cost effective strategies for the control of hydrocarbons requires that more stringent emissions reductions be applied to the more reactive organic compounds.^{10,11,19,26} This in turn has led to a continuing requirement for a rational assessment of hydrocarbon reactivity as a basis for control decisions. Such an assessment is particularly critical since attainment of the Federal air quality standard for photochemical oxidant has been sought largely through the stringent control of hydrocarbon emissions.^{27,28}

The first effort to formulate and apply a practical hydrocarbon reactivity scale was taken in 1966 with the implementation by the Los Angeles Air Pollution Control District (LAAPCD) of a regulation, known as Rule 66, to limit solvent organic emissions on the basis of their capacity for promoting photochemical smog formation.^{10,11} This rule and other conceptions of reactivity scales²⁹ represented a major advance in the application of the information then available concerning the mechanisms of photochemical smog formation to the development of practical air pollutant emission control strategies. Thus, the basic concept of selective control of emissions based on their reactivity is now widely established.

Not surprisingly however, there have been significant differences in hydrocarbon reactivity scales proposed by local, regional, and national air pollution control agencies^{25,30-34} as well as by industry.^{16,18,23} This in turn can lead to quite large differences in emission inventory estimates and in approaches to hydrocarbon control.^{30,35,36}

Most, although not all, previous reactivity classifications have relied primarily on smog chamber data obtained for relatively short irradiation (≤ 6 hrs) periods. Thus, the recent concern over oxidant formation resulting from longer irradiations during pollutant transport to regions downwind of urban sources introduces additional difficulties both in defining what constitutes a reactive hydrocarbon and in categorizing degrees of reactivity. For example, a compound such as propane, the major component in liquified petroleum gas (LPG) and often cited as a "clean" fuel, is now known³⁷⁻³⁹ to contribute to the formation of photochemical oxidants in the later stages of day-long irradiation periods. However, on the basis of data obtained during short-term irradiations, propane has been classified as "unreactive" in a reactivity scale

proposed²⁵ in 1974 by B. Dimitriades of the EPA (hereafter referred to as the EPA reactivity scale).

A third difficulty with reactivity scales which are based on previous smog chamber data concerns their reliance on measurements of smog manifestations such as maximum ozone concentrations. Observed values of such secondary properties of a photooxidation system can be significantly affected by the particular chamber materials, light source, purity of matrix air, and other aspects of the chamber methodology employed. This fact can account in large measure for the significant number of discrepancies which arise from comparison of the specific ranking of hydrocarbons in reactivity scales formulated on the basis of different sets of chamber data.

Altshuller and Bufalini^{9,20} have reviewed the various definitions of hydrocarbon reactivity and summarized results of numerous studies up to 1970. The criteria used for evaluating hydrocarbon reactivity include hydrocarbon consumption, the conversion of nitric oxide to nitrogen dioxide, ozone formation, aerosol formation, eye irritation and plant damage. It is generally agreed that the criteria most suitable with respect to photochemical oxidant control strategies are ozone dosage or maximum ozone concentration.³⁰ However, establishing a definitive hydrocarbon reactivity scale to be applied specifically to the control of ozone formation requires an extensive and lengthy experimental program in which the ozone-forming capability of each individual hydrocarbon is determined under simulated atmospheric conditions, including long-term irradiation (i.e., 10-12 hrs).

An alternative, and perhaps supplementary, basis for assessing hydrocarbon reactivity, which appears to have considerable utility and a valid experimental foundation, is the formulation of a reactivity scale based on the rate of disappearance of hydrocarbons due to their reaction with the hydroxyl radical, the key intermediate species in photochemical air pollution.

Results and Discussion

It is only comparatively recently that the critical role of OH in photochemical smog formation has been generally recognized⁴⁰⁻⁴⁴ and that appreciable rate constant data have become available for the reaction of OH with several classes of hydrocarbons. The importance of OH as a reactive intermediate relative to species such as O_3 , $O(^3P)$, and HO_2 has been shown previously⁴³⁻⁴⁶ through computer modeling of smog chamber data. For example, Niki, Daby, and Weinstock⁴³ showed that the reactivity of a number of hydrocarbons, as measured by the rate of conversion of NO to NO_2 , correlated significantly better with OH rate constants than with either $O(^3P)$ or O_3 rate constants.

The utility of a large environmental chamber in obtaining relative rate constants with an accuracy of $\pm 20\%$ for the reaction of the hydroxyl radical with a variety of hydrocarbons has been demonstrated in a number of recent studies both in this⁴⁵⁻⁴⁸ and other laboratories.⁴⁹ To date we have measured relative rates for the reaction of OH with some 35 organic compounds. The

detailed kinetic data derived from these investigations have been reported elsewhere.⁴⁵⁻⁴⁸ In these studies we determined the relative rates of disappearance of selected alkanes, alkenes and aromatic hydrocarbons under simulated atmospheric conditions of temperature, pressure, concentrations, light intensity and other trace contaminants (NO_x , CO, hydrocarbons, water). These relative rate constants were placed on an absolute basis using the published rate constants for OH + n-butane or isobutene. The assumption that OH was responsible for the hydrocarbon disappearance under the experimental conditions employed was subsequently supported by the very good agreement between OH rate constants determined for the individual compounds using flash photolysis-resonance fluorescence techniques^{50,51} and those obtained in our initial chamber experiments.^{45,46}

The importance of the chamber method for the purposes of formulating a reactivity scale is that it permits the simultaneous determination of valid rate constants for reactions of OH with a large number and wide variety of atmospherically important hydrocarbons. This substantially expands the number of compounds which can be incorporated, now and in the near future, in the resulting reactivity scale.

Use of OH Rate Constants as a Reactivity Index

From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in chamber simulations at the SAPRC⁴⁵⁻⁴⁸ and Ford⁴⁹ laboratories we conclude that, to a good approximation, this correlation can be extrapolated to the atmosphere (a) for alkenes in ambient air parcels during the early morning hours when ozone levels are generally quite low (≤ 0.05 ppm), and (b) for alkanes and aromatics at essentially all times and locations. The latter assumption, namely that an OH rate constant is a good "reactivity index" for alkanes and aromatics throughout an irradiation day (or multiple irradiation days) rests upon the fact that the rates of reaction of these classes of hydrocarbons with species such as ozone, $\text{O}(^3\text{P})$ atoms and the hydroperoxyl radical are several orders of magnitude slower than with OH.^{8,52-54} For example, even at the highest ozone concentrations experienced in ambient atmospheres, O_3 will not contribute significantly to the photooxidation of alkanes and aromatics. This is in contrast to the case for alkenes which, although the rate constants for reaction of O_3 with alkenes are not particularly large,⁵⁵⁻⁵⁷ react rapidly with ozone at the average concentrations commonly encountered in polluted ambient air (~ 0.1 - 0.2 ppm).

Proposed Reactivity Scale

Under the assumption that hydrocarbon depletion is due solely to attack by OH (with the qualification noted for alkenes), we propose a five-class reactivity scale based on hydrocarbon disappearance rates due to reaction with OH. The ranges of reactivities for the five proposed classes each span an order of magnitude in reactivity relative to methane and are shown in Table I. Although a scale based on OH rate constants can be divided into an arbitrary number of classes, we have found it convenient and useful (particularly for purposes of

comparison with other scales) to employ the order of magnitude divisions which lead to a five-class scale.

The hydrocarbon half-lives (defined as $t_{1/2} = 0.693/k[\text{OH}]$) corresponding to each class are also shown in Table I. These half-lives were calculated assuming depletion of the hydrocarbon solely due to reaction with the hydroxyl radical, and assuming an OH radical concentration in polluted atmospheres of 10^7 radicals cm^{-3} , a reasonable value on the basis of both model calculations⁵⁸ and recent atmospheric measurements.⁵⁹⁻⁶¹

Table II shows the compounds, for which OH rate constants have been found or calculated, distributed among the five classes of our proposed reactivity scale in the order of increasing rates of reaction within each class. Employing OH rate constants obtained from hydrocarbon disappearance rates measured in photooxidation studies^{62,63} as well as those from elementary rate determinations and our chamber studies, has permitted tabulation of OH rate constant data for 80 hydrocarbons. These 80 hydrocarbons are incorporated in Table II.

For interest, carbon monoxide although not a hydrocarbon, is included in Table II, since it is present in polluted urban atmospheres. Although CO is generally regarded as being "unreactive" in ambient air, in our scale it appears in Class II, which also includes ethane and acetylene.

In our current compilation of compounds, methane is the only compound listed which appears in Class I, although the recent work of Chameides and Stedman has shown that even methane will react given sufficient time.⁶⁴ Most of the straight chain alkenes appear in Class IV with the substituted alkenes occurring in the upper half of Class IV and in Class V. The alcohols fall into Class III while the monoterpene hydrocarbons are highly reactive and most of them appear in Class V with α - and β -pinene occurring in the upper half of Class IV. The reactivity classification shown in Table II is similar to an earlier one we have formulated,⁶⁵ but many more compounds have now been included.

Comparison with Other Scales

The ranking of reactivities for the aromatic hydrocarbons in our scale is essentially the same as that obtained by Altshuller et al.⁴ and by Kopczynski.^{7,66} Although our proposed scale is based solely on hydrocarbon disappearance rates, Altshuller and Bufalini²⁰ have shown that this measure of reactivity is very similar to the one based on nitric oxide oxidation rates. They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and Cohen⁶ and Glasson and Tuesday⁸ was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle,² Stephens and Scott,³ and Tuesday.⁵

As indicated above, Rule 66 formulated by the LAAPCD in 1966 represented the first hydrocarbon control measure based on photochemical reactivity. Although this and similar regulations have been effective, results from recent

studies³⁷⁻³⁹ indicate that they give insufficient recognition to the ozone-forming potential of slow reactors, such as n-butane and propane under long-term irradiation conditions. Consequently, it is now realized that measures more stringent than Rule 66 are necessary to achieve reductions in ozone formation to levels approaching those mandated by the U. S. Clean Air Act Amendments of 1970.

Recognition of such deficiencies in current hydrocarbon control regulations has led to re-examination of present hydrocarbon reactivity classifications. The focus of these re-evaluations has been the five-class reactivity scale (see Table III) proposed by B. Dimitriadis at the EPA Solvent Reactivity Conference in 1974.²⁵ Significant changes have been suggested for this reactivity classification by the California ARB,³⁰⁻³³ the LAAPCD,³⁴ the EPA,⁶⁷ and by industry. The EPA is currently examining this question and since no final conclusions have been reached at this time, we will restrict comparison of our proposed scale to the scale proposed in 1974 by Dimitriadis of the EPA. In addition, we will discuss our proposed scale in the context of the three-class system recently approved³² by the ARB for application to hydrocarbon pollutant inventories and for planning future control strategies.

Briefly, the EPA has proposed, on the basis of previous experimental studies, that methane, ethane, acetylene, propane, and benzene are essentially non-reactive for typical urban ambient hydrocarbon-NO_x ratios²⁵ and these compounds are placed in Class I on their scale. Three other classes have been proposed for mobile source hydrocarbon emissions⁶⁸—Class III (C₄ and higher alkanes), Class IV (aromatics less benzene) and Class V (alkenes). When stationary source hydrocarbons, including solvents (Class II), are added to the list, five classes are suggested as shown in Table III.

The reactivity classification proposed here (Tables I, II) can be compared with that suggested by the EPA (Table III). It is evident that several significant differences emerge:

- (1) The C₁-C₃ alkanes are given equal weighting in the EPA scale and all are designated unreactive, while our scale clearly differentiates between the three compounds methane, ethane, and propane in Classes I, II, and III, respectively.
- (2) According to our proposed classification, benzene and n-butane are of similar reactivity, while the EPA scale places them in Class I and III, respectively.
- (3) All the alkenes are placed in Class V of the EPA scale, while our proposed scale shows a differentiation in reactivity from ethene in Class III to 2,3-dimethyl-2-butene in Class V.
- (4) Our scale gives recognition to the high reactivity of natural hydrocarbons such as the pinenes and d-limonene, placing these in Class IV and V, respectively. The present published EPA scale does not give a classification for natural hydrocarbons, although they could be loosely categorized as substituted alkenes in Class V.

In addition to noting these differences, some similarities exist between the two scales. For example, our scale shows that 1,3-butadiene is highly reactive which is consistent with previous studies indicating it to be a facile precursor of eye irritants²⁰ and highly effective in producing oxidant during irradiation of HC-NO_x mixtures.¹ Both our scale and the EPA's show methanol to be relatively unreactive, with a greater reactivity exhibited by the higher alcohols, although our scale predicts a lower overall reactivity than that of the EPA.

The three-class system recently approved by the ARB is shown in Table IV and is similar to one being considered by the EPA.³⁰ According to the ARB,³²

"Class I would include low reactivity organic compounds yielding little, if any, ozone under urban conditions. Class II would consist of moderately reactive organic compounds which give an intermediate yield of ozone within the first day of solar irradiation. Class III would be limited to highly reactive organic compounds which give very high yields of ozone within a few hours of irradiation."

In general, the three-class ARB scale is in line with the scale presented here, based on OH rate constants, with only minor exceptions. For example, the ARB scale shows the primary and secondary C₂+ alcohols to be highly reactive in Class III, while our scale shows them to be of moderate reactivity.

Finally, we wish to note two limitations of the reactivity scale proposed here. One limitation of our scale is that it is not strictly applicable to compounds which undergo significant photodissociation in the atmosphere, and aldehydes have been omitted for this reason. In such cases, the compound will be more reactive than predicted from a scale based on hydrocarbon depletion due solely to reaction with OH. A second limitation in the application of our scale concerns the inherent problem arising from uncertainties in the identity and fates of subsequent products.³³

Conclusion

Our proposed reactivity scale based on the depletion of hydrocarbons by reaction with the OH radical has utility in assessing hydrocarbon chemical behavior in polluted ambient air. Since only those organic compounds which participate in atmospheric reactions are of consequence in the chemical transformations in ambient air, their relative reactivity towards OH is a useful and directly measurable index of their potential importance in the production of secondary pollutants.

One advantage of the proposed scale is that, because it is based on the individual rate constants for hydrocarbon reaction with OH, any degree of gradation in reactivity may be used to formulate any desired number of classes--from relatively few to a large number of classes or even an ordered ranking of compounds. A second strength of the present scale is that it can be readily extended to include additional organic compounds once their rate of reaction

with OH is known. Finally, the proposed scale gives adequate weight to alkanes and a number of aromatic hydrocarbons which require a significant period of time to react but can contribute substantially to ozone formation during longer irradiation periods, e.g., during their transport downwind from urban centers--a phenomenon of increasing concern to air pollution control agencies.

Acknowledgement

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Table I. Reactivity Scale for Hydrocarbons Based on Rate of Disappearance of the Hydrocarbon due to Reaction with the Hydroxyl Radical.

Class	Half-life ^a (days)	Reactivity Relative to Methane (= 1)
I	≥ 10	≤ 10
II	1 - 10	10 - 100
III	0.1 - 1	100 - 1000
IV	0.01 - 0.1	1000 - 10,000
V	≤ 0.01	$\geq 10,000$

^a $t_{1/2} = 0.693/k_{OH}[OH]$. $[OH]$ is assumed to be 10^7 radicals cm^{-3} .

Table II. Proposed Reactivity Classification of Hydrocarbons and CO Based on Reaction with the Hydroxyl Radical

CLASS I ($\leq 4.8 \times 10^7$) ^a	CLASS II ($4.8 \times 10^7 - 4.8 \times 10^8$) ^a	CLASS III ($4.8 \times 10^8 - 4.8 \times 10^9$) ^a	CLASS IV ($4.8 \times 10^9 - 4.8 \times 10^{10}$) ^a	CLASS V ($\geq 4.8 \times 10^{10}$) ^a
Methane	Methanol Carbon monoxide Acetylene Ethane	Neopentane Cyclobutane 2,2,3,3-Tetramethylbutane Benzene Ethyl acetate Isobutane Propane Diethyl ketone Isopropyl acetate n-Butane n-Butyl acetate Ethanol Methylethyl ketone Isopentane 1-Propanol 2,2,4-Trimethylbutane 2,3-Dimethylbutane 2,2,3-Trimethylbutane Tetrahydrofuran 2-Methylpentane Toluene Cyclopentane n-Propylbenzene Isopropylbenzene Ethene n-Hexane Cyclohexane n-Pentane p-Menthane 1-Butanol Isopropyl alcohol 4-Methyl-2-pentanol 3-Methylpentane Ethylbenzene	n-Octane Diethyl ether p-Xylene p-Ethyltoluene o-Ethyltoluene o-Xylene p-Cymene Methyl isobutyl ketone Di-n-propyl ether m-Ethyltoluene m-Xylene 1,2,3-Trimethylbenzene Propene 1-Butene 3,3-Dimethyl-1-butene 1-Pentene 1-Hexene 1,2,4-Trimethylbenzene Isobutene 1,3,5-Trimethylbenzene cis-2-Butene Diisobutyl ketone 2-Methyl-1-butene α-Pinene Cyclohexene cis-2-Pentene trans-2-Butene β-Pinene 1,3-Butadiene Isoprene	2-Methyl-2-butene 3-Carene 2,3-Dimethyl-2-butene β-Phellandrene Carvomenthene d-Limonene Dihydromyrcene Myrcene cis-Ocimene

^a Range of values (in liter mole⁻¹ sec⁻¹) for the rate constant for reaction of the OH radical with the listed compounds.

Table III. Proposed EPA Reactivity Classification of Organics (from reference 25, 1974)

CLASS I (Nonreactive)	CLASS II (Reactive)	CLASS III (Reactive)	CLASS IV (Reactive)	CLASS V (Reactive)
C ₁ -C ₃ paraffins	Mono-tertiary-alkyl benzenes	C ₄ + paraffins	Primary & Secondary alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins		α-Methyl styrene
Benzene		Styrene	Dialkyl benzenes	Aliphatic aldehydes
Benzaldehyde	Tertiary-alkyl acetates	n-Alkyl ketones	Branched alkyl ketones	Tri- & tetra-alkyl benzenes
Acetone	2-nitropropane	Primary & Secondary alkyl acetates	Primary & Secondary alkyl alcohols	Unsaturated ketones
Methanol		N-methyl pyrrolidone	Cellosolve acetate	Diacetone alcohol
Tertiary-alkyl alcohols		N,N-dimethyl acetamide	Partially halogenated olefins	Ethers
Phenyl acetate		Partially halogenated paraffins		Cellosolves
Methyl benzoate				
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons				
REACTIVITY RATING: 1.0	3.5	6.5	9.7	14.3

Table IV. California Air Resources Board (ARB) Reactivity Classification of Organic Compounds³²

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C ₁ -C ₂ Paraffins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic Ketones	All Olefinic hydrocarbons (including partially halogenated)
Benzene	Alkyl acetates	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	Branched alkyl Ketones
Acetone	C ₃₊ Paraffins	Cellosolve acetate
Methanol	Cycloparaffins	Unsaturated Ketones
Tert-alkyl alcohols	n-alkyl Ketones	Primary & Secondary C ₂₊ alcohols
Phenyl acetate	N-Methyl pyrrolidone	Diacetone alcohol
Methyl benzoate	N,N-dimethyl acetamide	Ethers
Ethyl Amines	Alkyl Phenols*	Cellosolves
Dimethyl formamide	Methyl phthalates**	Glycols*
Perhalogenated Hydrocarbons		C ₂₊ Alkyl phthalates**
Partially halogenated paraffins		Other Esters**
Phthalic Anhydride**		Alcohol Amines**
Phthalic Acids**		C ₃₊ Organic acids + di acid**
Acetonitrile*		C ₃₊ di acid anhydrides**
Acetic Acid		Formin**
Aromatic Amines		(Hexa methylene-tetramine)
Hydroxyl Amines		Terpenic hydrocarbons
Naphthalene*		Olefin oxides**
Chlorobenzenes*		
Nitrobenzenes*		
Phenol*		

*Reactivity data are either non-existent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable.

**Reactivity data are uncertain.

RELATIVE RATE CONSTANTS FOR THE REACTIONS OF OH RADICALS WITH ISOPROPYL ALCOHOL, DIETHYL AND DI-*n*-PROPYL ETHER AT 305 ± 2 K

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Relative rate constants have been obtained for the reaction of the hydroxyl radical (OH) with isopropyl alcohol and diethyl and di-*n*-propyl ether in environmental chamber photooxidation studies employing hydrocarbon- NO_x mixtures in air at 1 atmosphere and 305 ± 2 K. These results were obtained from measurements of the relative rates of disappearance of these compounds on the previously validated basis that OH radicals are dominantly responsible for their disappearance in the initial stages of reaction under the experimental conditions employed. Absolute rate constants, obtained by using the published rate constant for OH + isobutene of $3.05 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$ are ($k \times 10^{-9} \text{ l mole}^{-1} \text{ s}^{-1}$): isopropyl alcohol, 4.3 ± 1.3 ; diethyl ether, 5.6 ± 1.1 ; and di-*n*-propyl ether, 10.4 ± 2.1 . No previous determinations of these rate constants have been reported.

1. Introduction

The hydroxyl radical plays a fundamental role in chemical transformations in photochemical air pollution [1-7]. With the realization of the importance of OH has come an extensive experimental effort to determine rate constants for the reaction of OH with a large number of organic compounds. These studies have been documented in recent reviews [7] and in a critical compilation [8].

To date, however, comparatively few data have been obtained for the gas phase reactions of OH with oxygenated hydrocarbons [9-11]. In this work, rate constants are reported for the reaction of OH with three ingredients of commercial solvents [12,13] — isopropyl alcohol and diethyl and di-*n*-propyl ether. Such data are of fundamental importance in assessing the role of these oxygenated hydrocarbons in atmospheric chemistry, particularly since, as controls on automobiles reduce the contribution of hydrocarbons from mobile sources, emissions of such oxygenates from stationary sources become increasingly of greater concern.

2. Experimental

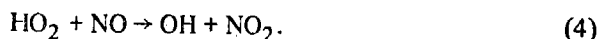
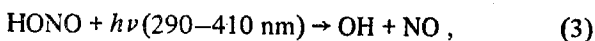
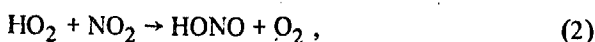
The technique used to determine relative OH rate constants in this study has been previously employed to obtain kinetic data for reactions of OH with alkanes [14,15], alkenes [11,15], ketones [11], aromatics [14,15], and halogenated [11,16] and natural hydrocarbons [11]. Briefly, irradiations of the hydrocarbon- NO_x -air system were carried out in a Pyrex chamber of approximately 6400-liter volume at a light intensity, measured as the rate of NO_2 photolysis in nitrogen (k_1), of 0.4 min^{-1} . All gaseous reactants were injected into pure matrix air [17] in the chamber using 100-ml precision bore syringes. Liquid reactants were injected with micropipettes. During irradiation, the chamber temperature was maintained at 305 ± 2 K.

The alcohol and ether concentrations were monitored with gas chromatography (FID), using a 5-ft. \times 1/8-in. stainless steel column packed with Poropak Q (80-100 mesh), operated at 393 and 423 K, respectively. Ozone was monitored by means of ultraviolet absorption; CO, by gas chromatography; and NO - NO_2 - NO_x , by the chemiluminescent reaction of NO with ozone.

The initial concentrations of reactant were isopropyl alcohol, 60 ppb (1 ppb in air $\equiv 4.0 \times 10^{-11}$ mole liter $^{-1}$ at 305 K and 1 atmosphere); diethyl ether, 20 ppb; and di-*n*-propyl ether, 55 ppb. In addition to these compounds, traces of several alkanes, alkenes and oxygenates were present [11,15]. Initial concentrations in these experiments were 800–1500 ppbC of total non-methane hydrocarbons, 0.60 ppm of NO_x (with an NO_2/NO_x ratio of 0.03–0.08), 6 ppm of CO, and 3000 ppb of methane, together with water vapor at 50% relative humidity. Replicate 3-hour irradiations were carried out with continuous analysis of inorganic species, analysis of hydrocarbons every 15 minutes, and analysis of isopropyl alcohol and the ethers every 30 minutes.

All data were corrected for losses due to sampling from the chamber by subtraction of the average dilution rate (1.2–1.6% per hour) from the observed hydrocarbon disappearance rate. The HC/ NO_x and NO/NO_2 ratios were chosen to delay the formation of ozone, and ozone was not detected during the irradiation period [11,14].

As discussed in detail previously [11,15], the major sources of OH in our experimental system are probably the photolysis of HONO and the reaction of HO_2 with NO [5,6,18,19];



The first reaction is thought to occur relatively slowly homogeneously [20,21], but its rate is probably significantly faster when the reaction is catalyzed by surfaces. Thus, nitrous acid has been observed in a chamber study of simulated atmospheres carried out in our laboratory [22], while direct evidence for formation of OH radicals in an environmental chamber has been provided recently by Niki, Weinstock and co-workers [23,24].

The concentration of OH radicals present during these irradiation experiments was calculated to range from 1.4 to 3.5×10^6 radicals cm^{-3} , depending upon the conditions of the specific experiment. The calculations employed the observed rates of isobutene dis-

appearance (corrected for dilution) and the previously determined rate constant for OH + isobutene [25]. These concentrations are the same order as those calculated [18,26,27] and observed directly [23,24,28, 29] by other workers.

3. Results and discussion

Typical rates of disappearance observed during the irradiations of isopropyl alcohol and of the two ethers are shown in figs. 1 and 2, respectively. Isobutene was used as the reference compound and is included in the figures. From these pseudo-first-order rates of disappearance of the hydrocarbons, rate constants relative to that of isobutene were obtained for the reaction of the PH radical with isopropyl alcohol and diethyl and di-*n*-propyl ether. These were placed on an absolute basis, using a value of $3.05 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$ for the reaction of OH with isobutene [25]. These results are presented in table 1.

There are no rate constants currently available for the reaction of OH radicals with ethers. Assuming that hydrogen abstraction is the major reaction pathway, one would expect these rate constants to be larger than

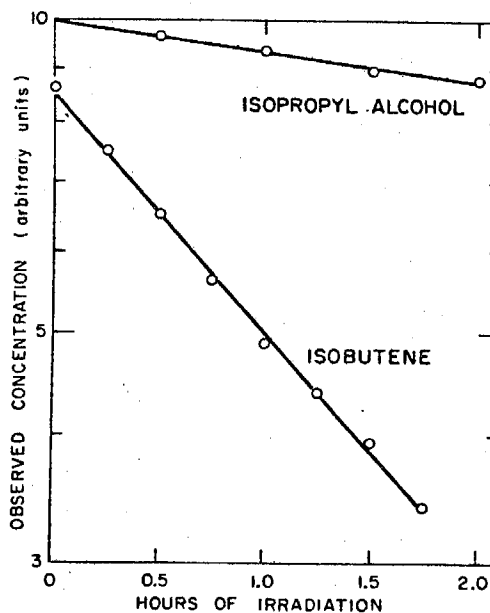


Fig. 1. Concentrations of isopropyl alcohol and isobutene (plotted on a logarithmic scale) during photolysis of HC- NO_x mixture in air at 305 ± 2 K and 1 atm.

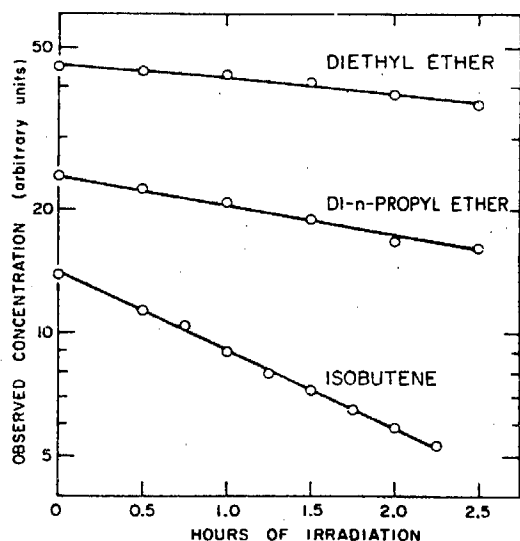


Fig. 2. Concentrations of diethyl and di-*n*-propyl ether and isobutene (plotted on a logarithmic scale) during photolysis of HC-NO_x mixture in air at 305 ± 2 K and 1 atm.

those for the corresponding alkane, since the C-H bond strengths in the ethers are at least several kilocalories weaker [30]. Thus, our rate constants (at 305 K) for diethyl and di-*n*-propyl ethers of 5.6 and $10.4 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$, respectively, compare with values for the corresponding alkanes, *n*-butane and *n*-hexane (at 298 K) of 1.6 and $2.9 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$, respectively, calculated from the formula of Greiner [31].

Two recent measurements of the rate constants for the gas phase reaction of OH radicals with alcohols

have been reported. Osif et al. [9] obtained a value of $5.3 \times 10^7 \text{ l mole}^{-1} \text{ s}^{-1}$ for OH + methanol using a value of $8.4 \times 10^7 \text{ l mole}^{-1} \text{ s}^{-1}$ for OH reaction with CO [8]. Recently, Campbell et al. [10] have carried out studies of the reaction of OH with a series of alcohols—methanol, ethanol, 1-propanol and 1-butanol. Our value for OH + isopropyl alcohol of $(4.3 \pm 1.3) \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ at 305 K is consistent with the value of $(2.3 \pm 0.2) \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ reported for 1-propanol by Campbell et al. [10] at 292 K.

Although, as mentioned, no literature data are available for the reaction of OH with ethers, it is interesting to examine the data for solvent photooxidations obtained by Laity et al. [32] in chamber studies. These workers irradiated separate solvent-NO_x-air mixtures in a stainless steel chamber at 305 K and reported the maximum rate of hydrocarbon disappearance observed in these experiments relative to toluene. If this disappearance is assumed to be predominantly due to attack by OH, then absolute rate constants may be derived from these data, using a value of $3.6 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ for the reaction of OH + toluene [33,34]. Values for OH + isopropyl alcohol and OH + diethyl ether are 3.1×10^9 and $5.4 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$, respectively, compared to our results of 4.3 and $5.6 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$. Considering the differences in experimental methods and apparatus, as well as the uncertainties involved in such an interpretation of the data of Laity et al. [32], the agreement obtained for isopropyl alcohol and diethyl ether is quite satisfactory. Similar treatment of their chamber data for other compounds for which the OH rate constants are known yields results [35] in fair agreement with literature values.

Table 1
Relative and absolute rate constants for the reaction of OH with selected hydrocarbons

Compound	Relative rate of disappearance	$k (\text{l mole}^{-1} \text{s}^{-1} \times 10^{-9})$	
		this work a)	literature
isobutene	1	30.5	
isopropyl alcohol	0.14	4.3	3.1 b)
diethyl ether	0.18 ₅	5.6	5.4 b)
di- <i>n</i> -propyl ether	0.34	10.4	

a) Using a literature value of $3.05 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$ for OH + isobutene [25].

b) Using the data of Laity et al. [32] and attributing the HC loss solely to reaction with OH; results placed on an absolute basis using a value of $3.6 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ for OH + toluene (see text).

The atmospheric half lives, $t_{1/2} = 0.693/k_{OH+RH} \times [OH]$, for isopropyl alcohol and diethyl and di-*n*-propyl ether are calculated to be 5.4, 4.1 and 2.2 hours, respectively, using an ambient OH concentration of 5×10^6 radicals cm^{-3} [18,23,24,26-29] and our rate constants. Thus, these compounds react with OH at rates similar to ethene, $\text{C}_6 - \text{C}_7$ alkanes, and mono-alkyl substituted benzenes [36]. The relative importance of alcohols, ethers and other oxygenated hydrocarbons in photochemical smog formation are discussed in detail elsewhere [35-37].

Acknowledgement

The authors gratefully acknowledge the assistance of F.R. Burleson in carrying out the gas chromatographic analyses, W.D. Long for valuable assistance in conducting the chamber experiments and Dr. R. Atkinson for useful comments concerning this manuscript. This work was supported in part by the California Air Resources Board (Contract No. ARB 5-385) and the National Science Foundation-Research Applied to National Needs (NSF-RANN Grant No. AEN73-02904-A02).

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RELATIVE RATE CONSTANTS FOR THE REACTION OF OH RADICALS WITH SELECTED C₆ AND C₇ ALKANES AND ALKENES AT 305 ± 2 K

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Measurements of the rates of disappearance of three alkenes and two alkanes relative to isobutene in environmental chamber photooxidation studies employing hydrocarbon-NO_x mixtures in air at 1 atmosphere have been used to obtain relative rate constants for the reaction of these compounds with the hydroxyl radical. Absolute rate constants at 305 ± 2 K obtained using a published rate constant for OH + isobutene of $3.05 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$ are ($k \times 10^{-9} \text{ l mole}^{-1} \text{ s}^{-1}$): cyclohexene, 47 ± 9 ; 1-methylcyclohexene, 58 ± 12 ; 1-heptene, 22 ± 5 ; 2,3-dimethylbutane, 3.1 ± 0.5 ; 2,2,3-trimethylbutane, 2.3 ± 0.5 . No previous determinations of OH rate constants have been reported for 1-heptene and 1-methylcyclohexene. For the remaining compounds these results are shown to be in good agreement with literature values reported for elementary, or relative rate constant determinations.

1. Introduction

Recently, we have reported rate constant determinations for the reaction of OH with alkanes [1, 2], alkenes [2, 3], aromatic hydrocarbons [1, 2], monoterpene hydrocarbons [3], halogenated hydrocarbons [3, 4], ketones [3], and ethers and isopropyl alcohol [5]. These rate constants were obtained by measuring the relative rates of disappearance of hydrocarbons in a hydrocarbon-NO_x mixture in air at 1 atmosphere and at 305 ± 2 K. Absolute rate constants were obtained [1-3, 5] by using literature values for OH + *n*-butane and/or isobutene, at least one of which was employed as a reference compound in each study. A similar technique has recently been employed by Niki and co-workers [6]. Results obtained from these relative rate studies have uniformly been in very good agreement with literature values reported for elementary rate constant determinations [7].

Here we report rate constant data at 305 ± 2 K for the reaction of OH with 1-heptene, 1-methylcyclohexene, cyclohexene, and two substituted alkanes — 2, 3-dimethylbutane and 2, 2, 3-trimethylbutane. These long-chain alkanes and cyclic alkenes have been suggested to play a major role in the formation of the organic portion of aerosols found in polluted ambient air [8, 9].

2. Experimental

The experimental technique used to determine relative OH rate constants in this study has been described in detail previously [1-3]. Briefly, irradiations of the hydrocarbon-NO_x-air system were carried out in a Pyrex chamber of approximately 6400-liter volume at a light intensity, measured as the rate of NO₂ photolysis in nitrogen (k_1), of 0.4 min^{-1} . During irradiation, the chamber temperature was maintained at 305 ± 2 K.

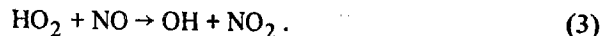
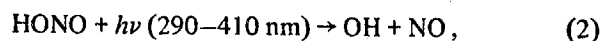
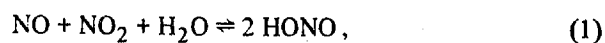
The alkane and alkene concentrations were monitored with gas chromatography (FID), using a 5' × 1/8" SS of Poropak Q (80-100 mesh) column and a 36' × 1/8" SS column of 10% dimethylsulfolane on AW C-22 Firebrick (60-80 mesh) followed by 18" × 1/8" SS column of 10% Carbowax 600, operated at 433 and 273 K, respectively. Ozone was monitored by means of ultraviolet absorption; CO by gas chromatography, and NO-NO₂-NO_x by the chemiluminescent reaction of NO with ozone.

The initial concentrations of reactants were 2, 3-dimethylbutane, 7 ppb (1 ppb in air $\equiv 4.0 \times 10^{-11} \text{ mole liter}^{-1}$ at 305 K and 1 atmosphere); 2, 2, 3-trimethylbutane, 14 ppb; cyclohexene, 10 ppb; 1-methylcyclohexene, 21 ppb, and 1-heptene, 14 ppb. In addition to these compounds, traces of several alkanes, alkenes, and oxygenates were present [2, 3]. Initial

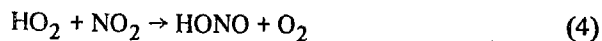
concentrations in these experiments were 700–800 ppbC of total non-methane hydrocarbons, 0.61 ppm of NO_x (with an NO_2/NO_x ratio of 0.04–0.05), 6 ppm of CO, and 2900 ppb of methane, together with water vapor at 50% relative humidity. Replicate three-hour irradiations were carried out with continuous analysis of inorganic species and analysis of hydrocarbons every 30 minutes.

All data were corrected for losses due to sampling from the chamber by subtraction of the average dilution rate (1.6% per hour) from the observed hydrocarbon disappearance rate. The HC/NO_x and NO/NO_2 ratios were chosen to delay the formation of ozone, and ozone was not detected during the irradiation period [1, 3].

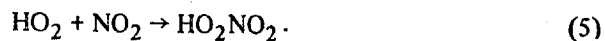
As discussed in detail previously [2, 3], the major sources of OH in our experimental system are probably the photolysis of HONO and the reaction of HO_2 with NO [10–13]:



The first reaction is thought to occur relatively slowly homogeneously [14–16], but its rate is probably significantly faster when the reaction is catalyzed by surfaces. Thus, nitrous acid has been observed in a chamber study of simulated atmospheres carried out in our laboratory [17], while direct evidence for formation of OH radicals in an environmental chamber has been provided recently by Niki, Weinstock and co-workers [6, 18, 19]. The reaction of HO_2 with NO_2 has also been proposed as a source



of nitrous acid [20, 21], but recent results [22, 23] suggest that peroxyxynitric acid is the major product of reaction (4).



The peroxyxynitric acid may decompose back to HO_2 and NO_2 , or possibly give HONO, but this is currently uncertain [22, 23].

The concentration of OH radicals present during these irradiation experiments was calculated to range

from $(2.5\text{--}5.0) \times 10^6$ radicals cm^{-3} depending upon the conditions of the specific experiment. The calculations of OH concentrations employed the observed rates of isobutene disappearance (corrected for dilution) and the previously determined rate constant for $\text{OH} + \text{isobutene}$ [24]. These concentrations are the same order as those calculated [12, 25, 26] and observed directly [18, 27, 28] by other workers.

3. Results and discussion

Isobutene was used as the reference compound in this series of experiments. From the pseudo-first-order rates of disappearance of the hydrocarbons, rate constants relative to that of isobutene were obtained for the reaction of the OH radical with 2, 3-dimethylbutane, 2, 2, 3-trimethylbutane, cyclohexene, 1-methylcyclohexene and 1-heptene. These were placed on an absolute basis using a value of $3.05 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$ for the reaction of OH with isobutene [24]. These results are presented in table 1, together with the available literature data.

Within the estimated 20% uncertainty in our rate constant values, the agreement among our data and the literature values is good. For example, our value of $(3.1 \pm 0.6) \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ for 2, 3-dimethylbutane agrees within experimental uncertainty with that of $(2.6 \pm 0.3) \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ recently determined in a separate study in this laboratory by Atkinson et al. [4]. This latter value was derived from the relative rates of disappearance of 2, 3-dimethylbutane and ethane during a 216-hour irradiation in the Pyrex chamber. Both of these values are significantly lower than the value directly determined by Greiner [29] at 300 K of $(5.16 \pm 0.13) \times 10^9$. However, it is expected [28] that the rate constant for the reaction of OH radicals with 2, 3-dimethylbutane would be less than twice as fast as with isobutane on the basis of the numbers of primary and tertiary hydrogen atoms in these two alkanes. The absolute rate constant for the reaction of OH radicals with isobutane has been determined to be $1.5 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ at 304 K [29], and hence the OH rate constant for 2, 3-dimethylbutane is expected to be $\leq 3 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$ which is in agreement with both the determination of Atkinson et al. [4] and with the present work.

Similarly, our value of $(2.3 \pm 0.5) \times 10^9 \text{ l mole}^{-1}$

Table 1

Relative and absolute rate constants for the reaction of OH and O(³P) with selected hydrocarbons

Compound	Relative rate of disappearance	$k(\ell \text{ mole}^{-1} \text{ s}^{-1} \times 10^{-10})$		
		$k_{\text{OH}} + \text{compound at 305 K}$		$k_{\text{O}(\text{P})} + \text{compound at 298 K}$
		this work ^{a)}	literature	
isobutene	1	3.05	—	1.2 ^{e)}
2,3-dimethylbutane	0.10	0.31 ± 0.06	0.45 b) , $0.26 \pm 0.03 \text{ c)}$	0.012 ^{e)}
2,2,3-trimethylbutane	0.074	0.23 ± 0.05	0.29 ^{b)}	—
1-pentene	—	—	$1.8 \pm 0.2 \text{ d)}$	0.28 ^{e)}
1-hexene	—	—	$1.9 \pm 0.2 \text{ d)}$	0.31 ^{e)}
1-heptene	0.73	2.2 ± 0.5	—	—
cyclohexene	1.53	4.7 ± 0.9	$3.8 \pm 0.4 \text{ d)}$	1.3 ^{e)}
1-methylcyclohexene	1.91	5.8 ± 1.2	—	$4.9 \pm 0.2 \text{ d)}$

^{a)} Using a literature value of $3.05 \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ for OH + isobutene [24].^{b)} Ref. [29], $T = 298 \text{ K}$. ^{c)} Ref. [4], $T = 305 \text{ K}$.^{d)} Ref. [16] using a literature value of $3.1 \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ at 303 K for OH + *cis*-2-butene [24].^{e)} Ref. [32]. ^{f)} Ref. [31].

s^{-1} for 2,2,3-trimethylbutane is in reasonable agreement with the value of $(2.9 \pm 0.1) \times 10^9 \ell \text{ mole}^{-1} \text{ s}^{-1}$ obtained by Greiner at 303 K [29]. In addition, the decrease in rate constant in going from 2,3-dimethylbutane to the larger molecule 2,2,3-trimethylbutane is consistent with a decrease from two to one in the number of tertiary hydrogen atoms [29]. These atoms are the most easily abstracted, since the C—H bond strength for tertiary hydrogens is 3 kcal mole^{-1} and 6 kcal mole^{-1} weaker than that for secondary and primary hydrogens, respectively [30].

Recently, Wu et al. [6] used a technique similar to the one employed here, namely, the photooxidation of hydrocarbons in the presence of NO_x in air at 1 atmosphere and 303 K. Under the assumption that OH was the principal species depleting the hydrocarbon, they obtained rate constants relative to *cis*-2-butene for several of the higher alkenes. Using a value of $3.1 \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ for OH + *cis*-2-butene at 303 K [24], one obtains a value of $3.8 \times 10^{10} \text{ mole}^{-1} \text{ s}^{-1}$ for cyclohexene at 303 K from the data of Wu et al. [6]. This value is in reasonable agreement with our value of $(4.7 \pm 0.9) \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ at 305 K.

Substitution of a methyl group for one of the hydrogen atoms in cyclohexene increases the rate constant slightly, since we obtain a value of $(5.8 \pm 1.2) \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ for 1-methylcyclohexene. This is expected by analogy with the similar

addition reaction of O(³P) atoms with cyclohexene and 1-methylcyclohexene (0.91 and 4.21 relative to O(³P) + cyclopentene) [31].

Table 1 shows a comparison of the reactivity of O(³P) atoms [31, 32] as well as OH radicals towards the compounds studied here and other selected compounds. Since both O(³P) and OH are expected to primarily undergo addition to the alkenes, one would expect the same trend in going from 1-pentene to cyclohexene and this is, in fact, observed. In addition, the value of $1.8 \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ obtained for 1-hexene by Wu et al. [6] and our value of $2.2 \times 10^{10} \ell \text{ mole}^{-1} \text{ s}^{-1}$ for 1-heptene, both obtained by similar methods, are consistent with the trend observed by Wu et al. [6] of an increase in rate constant with the larger molecular size of the alkene.

As mentioned above, the higher straight chain and cyclic alkenes are assumed to be important precursors of the organic content of ambient aerosols found in polluted air [9, 10]. The rapid rate of reaction of OH with these species ensures that, in addition to O_3 -alkene reactions, OH attack will be an important reaction pathway in real and simulated atmospheres, possibly yielding multifunctional oxygenated species in the aerosol phase [9, 33].

Assuming an ambient OH concentration of 5×10^6 radicals cm^{-3} [18, 27, 28], the atmospheric half-lives, $t_{1/2} = 0.693/k_{\text{OH}+\text{RH}}[\text{OH}]$, based solely on reaction

with OH, are (in hours): 2, 3-dimethylbutane, 7.5; 2, 2, 3-trimethylbutane, 10.0; cyclohexene, 0.49; 1-methylcyclohexene, 0.39; and 1-heptene, 1.0. In the case of the alkenes, the actual half-lives in the atmosphere are expected to be significantly less, since O_3 reacts with the alkenes at significant rates [9, 34].

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APPENDIX B

Inorganic and Hydrocarbon Data for
AGC Runs 216 through 223

AGC-216-1 SO2 DRY
GLASS CHAMBER
1976 JUL 27

DARK
FROM 1200 TO 1545 THE TEMPERATURES WERE TAKEN FROM THE LCG BOOK; FROM 1600 ON
THE TEMPERATURES WERE TAKEN FROM THE COMPUTER READOUT
TECO 43 SAMPLING RATE 1161 ML/MIN

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPH)
---------------	----------------------	----------------	----------------	--------------

1200	0.	29.4	1.0	0.359
1215	15.	29.4	0.0	0.353
1230	30.	29.6	0.0	0.359
1245	45.	29.6	3.0	0.355
1300	60.	29.6	2.5	0.355
1315	75.	29.6	2.0	0.344
1330	90.	29.4	2.0	0.357
1345	105.	29.6	2.0	0.344
1400	120.	29.7	2.0	0.342
1415	135.	29.7	1.5	0.344
1430	150.	29.7	1.5	0.349
1445	165.	29.7	2.0	0.335
1500	180.	29.7	1.5	0.330
1515	195.	29.9	1.5	0.338
1530	210.	30.0	1.5	0.329
1545	225.	26.7	1.5	0.331
1600	240.	*****	*****	*****
1615	255.	*****	*****	*****

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-216-2 SO2 DRY
GLASS CHAMBER
1976 JUL 27-28

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
---------------	----------------------	----------------	----------------	--------------

1630	270.	33.4	1.5	0.333
1646	286.	33.4	1.5	0.315
1701	301.	33.4	1.5	0.320
1716	316.	33.5	1.5	0.310
1731	331.	33.5	1.5	0.315
1746	346.	33.5	1.5	0.314
1800	360.	33.7	1.5	0.321
1815	375.	33.5	1.5	0.313
1830	390.	33.5	1.5	0.303
1845	405.	33.5	1.5	0.303
1900	420.	33.4	2.0	0.305
1915	435.	33.2	2.0	0.309
1930	450.	33.2	2.0	0.299
1945	465.	33.1	2.0	0.297
2000	480.	33.2	2.0	0.300
2015	495.	33.4	2.0	0.310
2030	510.	33.5	2.0	0.296
2045	525.	33.7	2.0	0.307
2100	540.	33.7	2.0	0.299
2115	555.	33.8	2.0	0.294
2130	570.	33.7	2.0	0.300
2145	585.	33.8	2.0	0.295
2200	600.	33.7	2.0	0.296
2215	615.	33.7	2.0	0.296
2230	630.	33.7	2.0	0.294
2245	645.	33.7	2.0	0.294
2300	660.	33.7	2.0	0.291
2315	675.	33.7	2.0	0.287
2330	690.	33.7	2.0	0.283
2345	705.	33.4	2.0	0.291
0	720.	33.4	2.0	0.285
15	735.	33.4	2.0	0.288

***** NO DATA TAKEN --- DATA DISCARDED ? QUESTIONABLE DATA

AGC-216-3 SO2 DRY
GLASS CHAMBER
1976 JUL 28

CLOCK TIME	ELAPSED TIME (MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
---------------	-----------------------	----------------	----------------	--------------

30	750.	33.9	2.0	0.287
45	765.	34.6	2.0	0.278
100	780.	35.0	2.0	0.280
115	795.	35.4	1.5	0.276
130	810.	35.4	1.5	0.281
145	825.	35.4	1.5	0.277
200	840.	35.4	1.5	0.277
215	855.	35.6	1.5	0.277
230	870.	35.6	1.5	0.281
245	885.	35.4	1.5	0.275
300	900.	35.6	1.5	0.270
315	915.	35.4	1.5	0.269
330	930.	35.6	1.5	0.271
345	945.	35.4	2.0	0.271
400	960.	35.4	1.5	0.261
415	975.	35.4	2.0	0.250
430	990.	35.4	2.0	0.264
445	1005.	35.3	2.0	0.264
500	1020.	35.4	2.0	0.260
515	1035.	35.3	2.0	0.250
530	1050.	35.3	2.0	0.254
545	1065.	35.4	2.0	0.250
600	1080.	35.1	2.0	0.252
615	1095.	35.0	2.0	0.249
630	1110.	35.0	2.0	0.248
645	1125.	35.0	2.0	0.249
700	1140.	35.0	2.0	0.249
715	1155.	35.0	2.0	0.243
730	1170.	35.0	2.0	0.244
745	1185.	35.0	2.5	0.239
800	1200.	34.7	2.5	0.238
815	1215.	34.7	2.5	0.238
830	1230.	34.5	2.5	0.236
845	1245.	34.5	2.5	0.241
900	1260.	34.7	2.5	0.237
915	1275.	34.7	2.5	0.230
930	1290.	34.7	2.5	0.236
945	1305.	34.7	2.5	0.231
1000	1320.	34.7	2.5	0.233
1015	1335.	34.7	2.5	0.232
1030	1350.	34.7	2.5	0.226
1045	1365.	34.7	2.5	0.225
1100	1380.	34.9	2.5	0.227
1115	1395.	34.9	2.5	0.220
1130	1410.	34.9	2.5	0.216
1145	1425.	34.7	2.5	0.215

AGC-217-1 SO2 LIGHT DRY
GLASS CHAMBER
1976 JUL 30

CONTINUATION OF AGC-216 LIGHTS ON JUL 29 AT 1000; INTENSITY 100%
DATA FOR 216-LIGHT USELESS DUE TO FAULTY DACS CHANNEL
SO2 STRIP CHART DATA USED FOR THIS RUN
2.5 ML CF SO2 INJECTED WITH 90 ML OF N2 ON JULY 30 AT 1003
DASIBI 1212 ON CHAMBER AT ABOUT 1534 TO 1537 ON JULY 30 AND FROM 1201 TO
1230 ON JULY 31
SAMPLING RATES (ML/MIN): TECO 43 - 1161; DASIBI 1212 - 600

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
1130	-15.	*****	*****	*****	0.328
1145	0.	*****	34.6	22.0	0.321
1200	15.	*****	35.1	21.5	0.315
1215	30.	*****	35.4	19.5	0.310
1230	45.	*****	35.6	18.0	0.307
1245	60.	*****	35.7	17.0	0.305
1300	75.	*****	36.0	16.5	0.301
1315	90.	*****	36.0	15.5	0.296
1330	105.	*****	36.1	14.5	0.292
1345	120.	*****	36.4	13.0	0.290
1400	135.	*****	36.6	11.0	0.286
1415	150.	*****	36.6	11.5	0.282
1430	165.	*****	36.5	11.5	0.279
1445	180.	*****	36.5	11.0	0.276
1500	195.	*****	36.2	11.0	0.273
1515	210.	*****	36.1	13.0	0.269
1530	225.	0.519	36.0	14.0	0.265
1545	240.	*****	35.8	15.0	0.262
1600	255.	*****	35.7	15.5	0.260
1615	270.	*****	35.7	16.0	0.255
1630	285.	*****	35.7	16.5	0.253
1645	300.	*****	35.7	17.0	0.250
1700	315.	*****	35.7	17.0	0.250
1715	330.	*****	35.7	18.0	0.247
1730	345.	*****	35.7	19.0	0.245
1745	360.	*****	35.6	20.0	0.242
1800	375.	*****	35.4	21.0	0.240
1815	390.	*****	35.4	22.5	0.237
1830	405.	*****	35.7	21.5	0.236
1845	420.	*****	36.1	19.0	0.235
1900	435.	*****	36.4	17.0	0.233
1915	450.	*****	36.5	16.0	0.230
1930	465.	*****	36.6	15.5	0.227
1945	480.	*****	36.6	14.5	0.225
2000	495.	*****	36.6	15.0	0.222
2015	510.	*****	36.6	15.0	0.220
2030	525.	*****	36.6	15.5	0.218
2045	540.	*****	36.6	15.5	0.216
2100	555.	*****	36.6	15.5	0.213
2115	570.	*****	36.5	16.5	0.211
2130	585.	*****	36.5	17.0	0.210
2145	600.	*****	36.5	17.5	0.208
2200	615.	*****	36.4	18.0	0.206
2215	630.	*****	36.4	18.0	0.204
2230	645.	*****	36.2	19.0	0.203
2245	660.	*****	36.4	19.5	0.200

2300	675.	*****	36.2	20.0	0.196
2315	690.	*****	36.2	20.5	0.195
2330	705.	*****	36.1	21.5	0.193
2345	720.	*****	36.1	22.5	0.190

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-217-2 SO2 LIGHT DRY
GLASS CHAMBER
1976 JUL 31

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
0	735.	*****	36.0	22.0	0.188
15	750.	*****	36.0	22.0	0.185
30	765.	*****	35.8	22.0	0.183
45	780.	*****	35.8	22.0	0.181
100	795.	*****	35.8	22.5	0.180
115	810.	*****	35.8	22.5	0.177
130	825.	*****	35.7	22.5	0.175
145	840.	*****	35.7	22.5	0.172
200	855.	*****	35.7	22.5	0.171
215	870.	*****	35.6	22.5	0.169
230	885.	*****	35.6	23.0	0.168
245	900.	*****	35.6	23.0	0.166
300	915.	*****	35.6	23.0	0.163
315	930.	*****	35.6	23.0	0.160
330	945.	*****	35.6	23.0	0.160
345	960.	*****	35.6	23.0	0.158
400	975.	*****	35.4	23.0	0.156
415	990.	*****	35.6	23.0	0.154
430	1005.	*****	35.6	23.5	0.152
445	1020.	*****	35.4	23.5	0.150
500	1035.	*****	35.4	23.5	0.148
515	1050.	*****	35.4	23.5	0.147
530	1065.	*****	35.4	23.5	0.145
545	1080.	*****	35.4	23.5	0.144
600	1095.	*****	35.4	23.5	0.142
615	1110.	*****	35.4	23.5	0.140
630	1125.	*****	35.4	24.0	0.139
645	1140.	*****	35.4	24.0	0.137
700	1155.	*****	35.4	24.0	0.135
715	1170.	*****	35.4	24.0	0.134
730	1185.	*****	35.4	24.0	0.133
745	1200.	*****	35.4	24.0	0.131
800	1215.	*****	35.3	24.0	0.129
815	1230.	*****	35.4	24.0	0.128
830	1245.	*****	35.4	24.5	0.127
845	1260.	*****	35.4	24.5	0.126
900	1275.	*****	35.4	24.5	0.124
915	1290.	*****	35.4	24.5	0.122
930	1305.	*****	35.4	24.5	0.120
945	1320.	*****	35.4	24.5	0.118
1000	1335.	*****	35.4	24.5	0.116
1015	1350.	*****	35.4	24.0	0.115
1030	1365.	*****	35.6	24.0	0.113
1045	1380.	*****	35.4	24.0	0.112
1100	1395.	*****	35.4	24.0	0.111
1115	1410.	*****	35.4	24.0	0.109
1130	1425.	*****	35.4	24.0	0.107
1145	1440.	*****	35.6	24.0	0.106
1200	1455.	*****	35.6	24.0	0.105
1215	1470.	0.504	35.4	24.0	0.103

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-1 SO2 40% RH
GLASS CHAMBER
1976 AUG 4

DARK

AT 0850 FC-12 AND SO2 WERE INJECTED INTO THE CHAMBER
THE DASI 1212 WAS ON THE CHAMBER FROM 1651 TO 1658
BRADY 1296, CALIBRATION 1976 JUL 16
SAMPLING RATES (ML/MIN): TECO 43 - 1233; DASI 1212 - 600;

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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1100	0.	*****	33.4	49.0	0.377
1105	5.	*****	33.4	48.5	0.381
1110	10.	*****	33.4	48.5	0.380
1115	15.	*****	33.4	46.0	0.379
1120	20.	*****	33.4	47.5	0.374
1125	25.	*****	33.5	47.0	0.375
1130	30.	*****	33.2	47.5	0.371
1135	35.	*****	33.4	47.0	0.372
1140	40.	*****	33.4	46.5	0.370
1145	45.	*****	33.4	46.0	0.371
1150	50.	*****	33.4	46.5	0.369
1155	55.	*****	33.4	46.5	0.364
1200	60.	*****	33.4	45.5	0.366
1205	65.	*****	33.5	45.0	0.367
1210	70.	*****	33.5	45.0	0.359
1215	75.	*****	33.5	45.0	0.362
1220	80.	*****	33.4	45.0	0.359
1225	85.	*****	33.4	44.0	0.362
1230	90.	*****	33.4	44.0	0.362
1235	95.	*****	33.4	44.5	0.355
1240	100.	*****	33.2	44.5	0.355
1245	105.	*****	33.2	44.0	0.353
1250	110.	*****	33.2	44.0	0.353
1255	115.	*****	33.4	44.0	0.352
1300	120.	*****	33.2	43.5	0.354
1305	125.	*****	33.4	43.0	0.351
1310	130.	*****	33.4	42.0	0.355
1315	135.	*****	33.4	42.0	0.348
1320	140.	*****	33.4	42.0	0.348
1325	145.	*****	33.5	41.5	0.352
1330	150.	*****	33.4	41.0	0.347
1335	155.	*****	33.5	42.0	0.344
1340	160.	*****	33.5	42.0	0.344
1345	165.	*****	33.4	41.5	0.344
1350	170.	*****	33.5	41.5	0.343
1355	175.	*****	33.5	42.0	0.343
1400	180.	*****	33.5	41.5	0.341
1405	185.	*****	33.7	40.5	0.341
1410	190.	*****	33.5	40.0	0.343
1415	195.	*****	33.5	41.0	0.340
1420	200.	*****	33.7	41.0	0.337
1425	205.	*****	33.7	40.5	0.338
1430	210.	*****	33.4	41.0	0.336
1435	215.	*****	33.7	42.0	0.336
1440	220.	*****	33.7	41.5	0.336
1445	225.	*****	33.5	41.5	0.332
1450	230.	*****	33.7	41.5	0.332
1455	235.	*****	33.7	42.0	0.330
1500	240.	*****	33.7	42.0	0.330
1505	245.	*****	33.7	42.0	0.330

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-2 S02 40% RH
GLASS CHAMBER
1976 AUG 4

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	S02 (PPM)
---------------	----------------------	----------------	----------------	----------------	--------------

1510	250.	*****	33.7	41.5	0.329
1515	255.	*****	33.7	42.0	0.325
1520	260.	*****	33.7	42.0	0.326
1525	265.	*****	33.7	42.0	0.325
1530	270.	*****	33.4	41.5	0.327
1535	275.	*****	33.5	42.0	0.324
1540	280.	*****	33.5	42.0	0.320
1545	285.	*****	33.4	43.0	0.322
1550	290.	*****	33.4	43.0	0.322
1555	295.	0.003	33.4	41.5	0.320
1600	300.	*****	33.4	42.0	0.322
1605	305.	*****	33.4	42.0	0.316
1610	310.	*****	33.4	42.5	0.319
1615	315.	*****	33.2	42.0	0.318
1620	320.	*****	33.4	42.5	0.314
1625	325.	*****	33.4	43.0	0.315
1630	330.	*****	33.5	43.0	0.315
1635	335.	*****	33.5	43.5	0.310
1640	340.	*****	33.5	44.0	0.313
1645	345.	*****	33.5	43.5	0.311
1650	350.	*****	33.5	44.0	0.309
1655	355.	*****	33.7	43.5	0.313
1700	360.	*****	33.5	44.5	0.308
1705	365.	*****	33.8	44.5	0.308
1710	370.	*****	33.8	44.0	0.308
1715	375.	*****	33.7	44.0	0.310
1720	380.	*****	33.8	43.5	0.303
1725	385.	*****	33.8	44.0	0.308
1730	390.	*****	33.8	44.0	0.303
1735	395.	*****	33.8	44.0	0.302
1740	400.	*****	33.8	43.0	0.302
1745	405.	*****	33.8	43.0	0.302
1750	410.	*****	33.8	43.0	0.293
1755	415.	*****	33.8	44.0	0.299
1800	420.	*****	33.8	43.5	0.296
1805	425.	*****	33.8	43.0	0.299
1811	431.	*****	33.7	43.0	0.294
1816	436.	*****	33.7	43.0	0.298
1821	441.	*****	33.7	43.5	0.297
1826	446.	*****	33.7	43.0	0.297
1831	451.	*****	33.7	43.5	0.296
1836	456.	*****	33.8	43.0	0.291
1841	461.	*****	33.7	43.5	0.292
1846	466.	*****	33.8	43.5	0.292
1851	471.	*****	33.8	42.5	0.292
1856	476.	*****	33.7	42.5	0.291

1901	481.	*****	33.8	43.0	0.289
1906	486.	*****	33.8	42.5	0.287
1911	491.	*****	33.7	42.0	0.288
1916	496.	*****	33.7	42.0	0.287

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-3 SO2 40% RH
GLASS CHAMBER
1976 AUG 4

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
1921	501.	*****	33.8	42.5	0.286
1926	506.	*****	33.8	42.0	0.285
1931	511.	*****	33.7	41.5	0.295
1936	516.	*****	33.7	42.5	0.295
1941	521.	*****	33.7	41.5	0.278
1946	526.	*****	33.7	41.5	0.282
1951	531.	*****	33.7	42.5	0.278
1956	536.	*****	33.7	42.0	0.278
2001	541.	*****	33.5	42.0	0.283
2006	546.	*****	33.5	42.5	0.277
2011	551.	*****	33.5	42.0	0.278
2016	556.	*****	33.4	41.5	0.277
2021	561.	*****	33.4	42.5	0.277
2026	566.	*****	33.4	42.5	0.276
2031	571.	*****	33.4	42.0	0.278
2036	576.	*****	33.4	42.5	0.275
2041	581.	*****	33.5	42.0	0.274
2046	586.	*****	33.5	42.0	0.275
2051	591.	*****	33.7	43.0	0.271
2056	596.	*****	33.5	42.5	0.271
2101	601.	*****	33.7	42.5	0.270
2106	606.	*****	33.5	43.0	0.271
2111	611.	*****	33.7	42.5	0.269
2116	616.	*****	33.7	42.5	0.270
2121	621.	*****	33.7	43.0	0.270
2126	626.	*****	33.7	42.0	0.270
2131	631.	*****	33.7	43.0	0.270
2136	636.	*****	33.7	42.5	0.267
2141	641.	*****	33.7	42.5	0.266
2146	646.	*****	33.7	43.0	0.265
2151	651.	*****	33.7	42.5	0.265
2156	656.	*****	33.5	42.5	0.269
2201	661.	*****	33.7	43.0	0.266
2206	666.	*****	33.5	42.5	0.263
2211	671.	*****	33.5	42.5	0.265
2216	676.	*****	33.7	43.0	0.264
2221	681.	*****	33.5	42.5	0.261
2226	686.	*****	33.5	43.5	0.263
2231	691.	*****	33.5	43.0	0.263
2236	696.	*****	33.5	42.5	0.259
2241	701.	*****	33.5	43.0	0.256
2246	706.	*****	33.5	42.5	0.258
2251	711.	*****	33.5	42.5	0.255
2256	716.	*****	33.5	43.0	0.256

***** NO DATA TAKEN

--- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-4 SO2 40% RH
GLASS CHAMBER
1976 AUG 4-5

ADD 660 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME (MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
2206	6.	33.5	42.5	0.263
2211	11.	33.5	42.5	0.265
2216	16.	33.7	43.0	0.264
2221	21.	33.5	42.5	0.261
2226	26.	33.5	43.5	0.263
2231	31.	33.5	43.0	0.263
2236	36.	33.5	42.5	0.259
2241	41.	33.5	43.0	0.256
2246	46.	33.5	42.5	0.253
2251	51.	33.5	42.5	0.255
2256	56.	33.5	43.0	0.256
2301	61.	33.5	42.5	0.254
2306	66.	33.5	42.5	0.255
2311	71.	33.5	43.0	0.250
2316	76.	33.7	42.5	0.250
2321	81.	33.5	43.0	0.250
2326	86.	33.5	43.0	0.252
2331	91.	33.4	42.0	0.249
2336	96.	33.5	43.0	0.250
2341	101.	33.5	42.5	0.252
2346	106.	33.5	42.0	0.245
2351	111.	33.5	42.5	0.248
2356	116.	33.4	42.0	0.248
1	121.	33.4	42.5	0.247
6	126.	33.4	42.5	0.250
11	131.	33.4	42.0	0.244
16	136.	33.4	42.5	0.245
21	141.	33.4	42.0	0.244
26	146.	33.4	42.0	0.244
31	151.	33.2	42.0	0.242
36	156.	33.4	41.5	0.242
41	161.	33.4	42.5	0.241
46	166.	33.2	42.0	0.239
51	171.	33.4	43.0	0.239
56	176.	33.2	43.0	0.239
101	181.	33.2	42.5	0.236
106	186.	33.2	43.5	0.236
111	191.	33.2	43.0	0.238
116	196.	33.1	43.0	0.236
121	201.	33.2	43.5	0.234
126	206.	33.2	43.0	0.233
131	211.	33.2	43.5	0.232
136	216.	33.2	43.0	0.233
141	221.	33.2	42.5	0.233
146	226.	33.2	43.5	0.233
151	231.	33.1	42.5	0.228

156	236.	33.2	43.5	0.228
201	241.	33.1	43.0	0.230
206	246.	33.1	43.5	0.230
211	251.	33.1	44.0	0.230

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-S SO2 40% RH
GLASS CHAMBER
1976 AUG 5

ADD 660 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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216	256.	33.1	43.0	0.231
221	261.	33.1	44.5	0.230
226	266.	33.0	43.5	0.227
231	271.	33.0	44.0	0.228
236	276.	33.0	44.5	0.228
241	281.	33.0	43.5	0.226
246	286.	33.0	44.5	0.225
251	291.	33.0	43.5	0.225
256	296.	33.0	43.5	0.223
301	301.	33.0	44.0	0.225
306	306.	32.8	43.5	0.225
311	311.	32.8	44.5	0.226
316	316.	32.7	43.5	0.222
321	321.	32.8	44.0	0.222
326	326.	32.8	43.5	0.221
331	331.	32.8	43.0	0.223
336	336.	32.8	43.5	0.220
341	341.	32.8	43.0	0.217
346	346.	32.8	44.0	0.220
351	351.	32.8	43.5	0.220
356	356.	32.7	44.5	0.217
401	361.	32.7	43.5	0.217
406	366.	32.7	44.0	0.216
411	371.	32.7	44.5	0.215
416	376.	32.6	43.5	0.217
421	381.	32.7	44.5	0.215
426	386.	32.6	44.0	0.213
431	391.	32.6	44.5	0.211
436	396.	32.6	44.0	0.211
441	401.	32.6	45.0	0.210
446	406.	32.4	44.0	0.211
451	411.	32.4	45.0	0.213
456	416.	32.4	44.5	0.210
501	421.	32.3	45.5	0.211
506	426.	32.3	44.5	0.210
511	431.	32.3	45.5	0.204
516	436.	32.3	44.5	0.209
521	441.	32.3	45.5	0.210
526	446.	32.3	44.5	0.208
531	451.	32.3	45.5	0.208
536	456.	32.3	44.5	0.204
541	461.	32.2	45.5	0.208
546	466.	32.2	44.5	0.205
551	471.	32.2	45.0	0.206
556	476.	31.6	45.0	0.210
601	481.	31.6	45.0	0.205

606	486.	31.6	45.5	0.203
611	491.	31.6	45.5	0.202
616	496.	31.6	45.0	0.202
621	501.	31.6	45.5	0.202

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-6 SO2 40% RH
GLASS CHAMBER
1976 AUG 5

ADD 660 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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626	506.	31.6	46.0	0.200
631	511.	31.6	45.5	0.200
636	516.	31.6	45.5	0.200
641	521.	31.6	46.0	0.199
646	526.	31.5	45.0	0.199
651	531.	31.6	45.5	0.199
656	536.	31.5	45.5	0.195
701	541.	31.8	45.0	0.197
706	546.	31.9	45.5	0.197
711	551.	31.9	45.5	0.195
716	556.	32.0	45.5	0.199
721	561.	32.2	46.0	0.197
726	566.	32.3	45.5	0.195
731	571.	32.4	46.0	0.194
736	576.	32.4	45.5	0.195
741	581.	32.4	45.5	0.193
746	586.	32.6	45.0	0.192
751	591.	32.7	45.5	0.194
756	596.	32.8	45.5	0.194
801	601.	33.0	45.5	0.193
806	606.	33.1	46.0	0.191
811	611.	33.1	45.0	0.191
816	616.	33.2	45.0	0.191
821	621.	33.2	45.5	0.192
826	626.	33.4	46.0	0.188
831	631.	33.4	45.5	0.188
836	636.	33.4	45.0	0.188
841	641.	33.5	45.0	0.188
846	646.	33.5	46.5	0.187
851	651.	33.5	45.5	0.186
856	656.	33.5	45.0	0.184

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

AGC-218-7 S02 404 PH

GLASS CHAMBER

1976 AUG 5

LIGHTS ON 0900; INTENSITY 100%

THE DASTI 1212 WAS ON THE CHAMBER: AUG5 0906 TO 0911, FROM 1 MIN TO 5 MIN AFTER
THE HOUR FROM 1000 TO 1005, 2047 TO 2130, 2201-2205; AUG 6 0707-0710

BE4BY 1296, CALIBRATION 1976 JUL 18

SAMPLING RATES (ML/MIN): TECO 43 - 1233; CASIFI 1212 - 600;

CLOCK ELAPSED CIONE 1151 REL HUM S02
TIME TIME(MIN) (PPM) (C/O C) (%) (PPM)

901	1.	*****	33.5	45.5	0.160
906	6.	*****	33.7	43.5	0.163
911	11.	0.035	34.2	35.5	0.161
916	16.	*****	34.5	40.5	0.158
921	21.	*****	34.4	46.0	0.177
926	26.	*****	34.9	44.5	0.170
931	31.	*****	35.0	44.0	0.159
936	36.	*****	35.1	43.5	0.172
941	41.	*****	34.9	42.5	0.173
946	46.	*****	34.7	43.0	0.170
951	51.	*****	34.5	42.0	0.168
956	56.	*****	34.5	41.5	0.166
1001	61.	*****	34.5	41.5	0.164
1006	66.	0.114	34.5	41.5	0.165
1011	71.	*****	34.7	41.5	0.164
1016	76.	*****	34.9	42.0	0.160
1021	81.	*****	34.5	42.0	0.158
1026	86.	*****	34.6	42.0	0.159
1031	91.	*****	34.5	41.0	0.156
1036	96.	*****	34.5	40.5	0.156
1041	101.	*****	34.6	40.5	0.153
1046	106.	*****	34.7	41.0	0.150
1051	111.	*****	34.7	40.5	0.144
1056	116.	*****	34.7	41.0	0.146
1101	121.	*****	34.5	41.0	0.151
1106	126.	0.170	34.6	40.5	0.153
1111	131.	*****	34.5	40.0	0.148
1116	136.	*****	34.5	39.5	0.145
1121	141.	*****	34.0	39.5	0.146
1126	146.	*****	34.0	39.0	0.147
1131	151.	*****	34.0	39.0	0.143
1136	156.	*****	34.6	39.0	0.142
1141	161.	*****	34.6	38.5	0.142
1146	166.	*****	34.6	37.5	0.135
1151	171.	*****	34.6	37.5	0.135
1156	176.	*****	34.5	37.0	0.140
1201	181.	*****	34.6	36.5	0.138
1206	186.	0.206	34.6	35.0	0.137
1211	191.	*****	34.9	35.0	0.137
1216	196.	*****	35.0	34.5	0.132
1221	201.	*****	34.4	34.0	0.133
1226	206.	*****	34.5	34.0	0.123
1231	211.	*****	34.7	33.5	0.124
1236	216.	*****	34.0	33.0	0.136
1241	221.	*****	34.5	33.5	0.125
1246	226.	*****	34.6	34.0	0.128

1251	231.	*****	34.0	33.5	0.125
1256	236.	*****	34.5	33.0	0.126
1301	241.	*****	34.5	33.5	0.128
1306	246.	0.239	34.5	33.5	0.126

***** NO DATA TAKEN

----- DATA DISCARDED

? NO SIGNIFICANT DATA

AGC-218-8 SO2 40% RH
GLASS CHAMBER
1976 AUG 5

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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1311	251.	*****	34.5	33.0	0.125
1316	256.	*****	34.5	33.5	0.129
1321	261.	*****	34.3	32.5	0.123
1326	266.	*****	34.7	33.5	0.123
1331	271.	*****	34.9	34.0	0.122
1336	276.	*****	34.7	34.0	0.122
1341	281.	*****	34.7	34.5	0.123
1346	286.	*****	34.7	34.5	0.120
1351	291.	*****	34.7	36.0	0.120
1356	296.	*****	34.6	36.0	0.118
1401	301.	*****	34.6	35.5	0.117
1406	306.	0.264	34.6	35.5	0.118
1411	311.	*****	34.6	34.0	0.118
1416	316.	*****	35.0	35.5	0.118
1421	321.	*****	35.1	36.0	0.117
1426	326.	*****	35.1	35.5	0.116
1431	331.	*****	35.0	33.5	0.114
1436	336.	*****	35.4	35.0	0.114
1441	341.	*****	35.4	35.5	0.111
1446	346.	*****	35.4	35.5	0.112
1451	351.	*****	35.3	35.0	0.110
1456	356.	*****	35.1	36.0	0.111
1501	361.	*****	35.1	34.5	0.110
1506	366.	0.287	35.0	34.5	0.109
1511	371.	*****	35.0	34.5	0.109
1516	376.	*****	34.9	34.0	0.109
1521	381.	*****	34.7	34.0	0.109
1526	386.	*****	34.7	35.5	0.107
1531	391.	*****	34.7	36.0	0.107
1536	396.	*****	34.6	36.5	0.104
1541	401.	*****	34.6	36.0	0.106
1546	406.	*****	34.6	36.5	0.104
1551	411.	*****	34.6	36.5	0.104
1556	416.	*****	34.6	36.5	0.104
1601	421.	*****	34.5	36.5	0.103
1606	426.	0.302	34.6	36.0	0.103
1611	431.	*****	34.5	36.5	0.103
1616	436.	*****	34.5	37.5	0.100
1621	441.	*****	34.5	37.0	0.100
1626	446.	*****	34.5	36.0	0.098
1631	451.	*****	34.5	36.0	0.099
1636	456.	*****	34.5	36.5	0.098
1641	461.	*****	34.5	37.0	0.098
1646	466.	*****	34.5	36.5	0.094
1651	471.	*****	34.5	37.0	0.094
1656	476.	*****	34.5	37.0	0.094

1701	481.	*****	34.5	36.0	0.095
1706	486.	0.315	34.5	36.0	0.094
1711	491.	*****	34.5	35.5	0.094
1716	496.	*****	34.5	34.5	0.092

***** NO DATA TAKEN

--- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-9 SO2 40% RH
GLASS CHAMBER
1976 AUG 5

AT 2059 PROPENE (6.4 ML) AND FC-12 (58.0 ML) WERE INJECTED

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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1721	501.	*****	34.5	34.0	0.092
1726	506.	*****	34.5	34.0	0.092
1731	511.	*****	34.5	34.5	0.092
1736	516.	*****	34.3	35.0	0.089
1741	521.	*****	34.3	33.5	0.089
1746	526.	*****	34.5	33.0	0.088
1751	531.	*****	34.6	31.0	0.087
1756	536.	*****	35.0	30.5	0.085
1801	541.	*****	35.1	32.0	0.085
1806	546.	0.313	36.0	33.0	0.084
1811	551.	*****	35.8	32.0	0.085
1816	556.	*****	35.8	32.0	0.081
1821	561.	*****	35.8	32.0	0.083
1826	566.	*****	36.0	31.5	0.083
1831	571.	*****	36.0	31.5	0.083
1836	576.	*****	36.0	32.0	0.081
1841	581.	*****	38.0	31.5	0.078
1846	586.	*****	38.0	32.0	0.081
1851	591.	*****	37.9	33.0	0.079
1856	596.	*****	37.7	33.5	0.078
1901	601.	*****	37.6	33.0	0.078
1906	606.	0.328	37.5	34.0	0.078
1911	611.	*****	37.5	33.5	0.078
1916	616.	*****	37.6	33.0	0.076
1921	621.	*****	37.6	33.0	0.077
1926	626.	*****	37.6	33.5	0.077
1931	631.	*****	37.6	34.0	0.074
1936	636.	*****	37.5	34.5	0.070
1941	641.	*****	37.2	34.5	0.074
1946	646.	*****	37.2	34.0	0.074
1951	651.	*****	37.2	34.0	0.074
1956	656.	*****	37.2	34.5	0.073
2001	661.	*****	37.0	35.0	0.071
2006	666.	*****	37.0	35.0	0.072
2011	671.	*****	36.9	35.5	0.071
2016	676.	*****	36.9	35.5	0.068
2021	681.	*****	36.0	36.0	0.068
2026	686.	*****	34.9	36.5	0.068
2031	691.	*****	34.9	36.5	0.070
2036	696.	*****	34.9	37.0	0.066
2041	701.	*****	35.0	37.0	0.066
2046	706.	*****	34.9	38.0	0.065
2051	711.	0.341	35.0	38.0	0.066
2056	716.	0.341	35.0	38.5	0.066
2101	721.	0.343	33.7	38.5	0.066

AGC-218-10 S02 40% RH
GLASS CHAMBER
1976 AUG 5-6

ADD 720 MIN TO ELAPSED TIME
AT 2059 PROPENE (6.4 ML) AND FC-12 (58.0 ML) WERE INJECTED
AT 2217 1.0 ML OF S02 WAS INJECTED

CLOCK TIME	ELAPSED TIME(MIN)	O2/N2 (PPM)	YS1 (DEG C)	REL HUM (%)	S02 (PPM)
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2106	6.	0.328	34.5	39.0	0.062
2111	11.	0.314	34.9	39.0	0.060
2116	16.	0.300	34.9	39.0	0.060
2121	21.	0.290	34.9	39.0	0.057
2126	26.	0.281	35.0	39.0	0.056
2131	31.	0.282	35.0	39.0	0.055
2136	36.	*****	35.0	39.0	0.056
2141	41.	*****	35.0	39.0	0.054
2146	46.	*****	35.0	39.0	0.054
2151	51.	*****	35.0	39.0	0.051
2156	56.	*****	35.0	39.0	0.053
2201	61.	*****	35.0	39.5	0.053
2206	66.	0.241	35.0	39.5	0.051
2211	71.	*****	35.0	39.0	0.051
2216	76.	*****	35.0	39.5	0.050
2221	81.	*****	33.8	39.0	0.216
2226	86.	*****	34.7	39.5	0.222
2231	91.	*****	34.9	39.5	0.222
2236	96.	*****	34.9	39.0	0.221
2241	101.	*****	35.0	39.0	0.217
2246	106.	*****	34.9	38.5	0.220
2251	111.	*****	34.9	39.0	0.220
2256	116.	*****	35.0	39.0	0.219
2301	121.	*****	34.9	39.0	0.216
2306	126.	*****	34.9	38.5	0.214
2311	131.	*****	34.9	38.5	0.213
2316	136.	*****	34.9	39.0	0.211
2321	141.	*****	34.7	39.0	0.209
2326	146.	*****	34.7	39.0	0.209
2331	151.	*****	34.7	38.5	0.206
2336	156.	*****	34.7	39.0	0.206
2341	161.	*****	34.7	39.0	0.204
2346	166.	*****	34.7	39.0	0.205
2351	171.	*****	34.7	38.5	0.204
2356	176.	*****	34.7	38.5	0.203
1	181.	*****	34.6	39.0	0.198
6	186.	*****	34.6	39.0	0.198
11	191.	*****	34.5	39.0	0.200
16	196.	*****	34.5	38.5	0.198
21	201.	*****	34.5	38.5	0.195
26	206.	*****	34.5	39.0	0.195
31	211.	*****	34.5	39.0	0.194
36	216.	*****	34.5	39.0	0.194
41	221.	*****	34.3	38.5	0.191
46	226.	*****	34.5	38.5	0.191
51	231.	*****	34.3	39.0	0.192

56	236.	*****	34.3	39.0	0.187
101	241.	*****	34.3	38.5	0.188
106	246.	*****	34.3	38.5	0.189
111	251.	*****	34.3	38.5	0.184

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

AGC-218-11 SO2 40% RH
GLASS CHAMBER
1976 AUG 6

ADD 720 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
116	256.	*****	34.3	38.5	0.183
121	261.	*****	34.3	38.5	0.184
126	266.	*****	34.3	38.0	0.182
131	271.	*****	34.2	38.5	0.181
136	276.	*****	34.2	38.5	0.182
141	281.	*****	34.2	38.0	0.180
146	286.	*****	34.2	38.0	0.177
151	291.	*****	34.2	38.0	0.176
156	296.	*****	34.2	38.5	0.177
201	301.	*****	34.2	38.0	0.176
206	306.	*****	34.2	38.0	0.175
211	311.	*****	34.2	38.0	0.172
216	316.	*****	34.2	38.5	0.173
221	321.	*****	34.2	38.5	0.171
226	326.	*****	34.1	38.5	0.169
231	331.	*****	34.1	38.5	0.169
236	336.	*****	33.9	39.0	0.165
241	341.	*****	33.9	38.5	0.170
246	346.	*****	33.9	38.5	0.170
251	351.	*****	33.9	38.5	0.165
256	356.	*****	33.9	39.0	0.167
301	361.	*****	33.9	38.5	0.166
306	366.	*****	33.9	38.5	0.164
311	371.	*****	33.9	38.5	0.161
316	376.	*****	33.9	38.5	0.161
321	381.	*****	33.9	38.0	0.160
326	386.	*****	33.8	38.0	0.161
331	391.	*****	33.8	38.5	0.161
336	396.	*****	33.8	38.5	0.158
341	401.	*****	33.8	38.0	0.159
346	406.	*****	33.8	38.5	0.156
351	411.	*****	33.8	38.5	0.156
356	416.	*****	33.8	38.0	0.156
401	421.	*****	33.8	38.5	0.151
406	426.	*****	33.8	38.5	0.153
411	431.	*****	33.8	38.0	0.153
416	436.	*****	33.8	38.0	0.150
421	441.	*****	33.8	38.5	0.151
426	446.	*****	33.8	38.0	0.149
431	451.	*****	33.8	38.0	0.150
436	456.	*****	33.8	38.5	0.145
441	461.	*****	33.7	38.5	0.148
446	466.	*****	33.8	38.5	0.143
451	471.	*****	33.7	39.0	0.145
456	476.	*****	33.8	39.0	0.144
501	481.	*****	33.7	38.5	0.148

506	486.	*****	33.8	38.5	0.143
511	491.	*****	33.7	38.5	0.140
516	496.	*****	33.8	38.0	0.142
521	501.	*****	33.8	38.0	0.139

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-218-12 SQZ 40S RH
GLASS CHAMBER
1978 AUG 5

ADD 720 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	SQZONE (PPM)	TS1 (DEG C)	SRL PPM (S)	SQZ (PPM)
526	506.	*****	33.8	38.0	0.137
531	511.	*****	33.8	37.5	0.140
536	516.	*****	33.8	38.0	0.137
541	521.	*****	33.8	37.5	0.137
546	526.	*****	33.8	37.0	0.138
551	531.	*****	33.7	37.0	0.134
556	536.	*****	33.7	37.0	0.134
601	541.	*****	33.7	37.0	0.133
606	546.	*****	33.7	36.5	0.133
611	551.	*****	33.8	36.5	0.134
616	556.	*****	33.7	36.5	0.132
621	561.	*****	33.8	36.5	0.132
626	566.	*****	33.8	37.0	0.129
631	571.	*****	33.7	37.0	0.131
636	576.	*****	33.8	37.0	0.129
641	581.	*****	33.7	37.0	0.132
646	586.	*****	33.7	37.0	0.126
651	591.	*****	33.7	37.0	0.127
656	596.	*****	33.7	36.5	0.126
701	601.	*****	33.7	37.0	0.127
706	606.	*****	33.7	37.0	0.125
711	611.	0.343	33.7	37.0	0.125
716	616.	*****	33.7	37.5	0.123
721	621.	*****	33.8	37.5	0.123
726	626.	*****	33.8	38.0	0.123
731	631.	*****	33.7	37.5	0.121
736	636.	*****	33.7	38.5	0.122
741	641.	*****	33.7	38.5	0.120
746	646.	*****	33.7	38.5	0.120
751	651.	*****	33.7	39.0	0.122
756	656.	*****	33.7	39.0	0.116
801	661.	*****	33.8	39.0	0.116
806	666.	*****	33.7	39.5	0.116
811	671.	*****	33.8	39.0	0.117
816	676.	*****	33.8	38.0	0.117
821	681.	*****	34.2	38.0	0.111
826	686.	*****	34.2	38.5	0.116
831	691.	*****	34.2	39.5	0.114

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

AGC-218-13 SQ2 40% RH
GLASS CHAMBER
1976 AUG 6

ADD 1410 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SQ2 (PPM)
829	-1.	*****	34.2	39.0	0.114
836	6.	*****	33.9	39.0	0.115
841	11.	*****	33.9	39.5	0.114
846	16.	*****	33.8	40.0	0.112
851	21.	*****	33.7	40.0	0.116
856	26.	*****	33.7	40.0	0.112
901	31.	*****	33.7	39.0	0.112
906	36.	*****	33.8	38.0	0.110
911	41.	*****	34.1	37.0	0.109
916	46.	*****	34.3	37.0	0.107
921	51.	*****	34.5	36.5	0.106
926	56.	*****	34.7	36.5	0.105
931	61.	*****	34.7	38.0	0.104
936	66.	*****	34.5	38.5	0.103
941	71.	*****	34.5	38.5	0.104
946	76.	*****	34.3	38.5	0.105
951	81.	*****	34.2	38.5	0.104
956	86.	*****	34.1	38.5	0.103
1001	91.	*****	33.9	38.0	0.103
1006	96.	*****	33.9	37.5	0.105
1011	101.	*****	33.9	37.5	0.101
1016	106.	*****	33.9	38.0	0.099
1021	111.	*****	33.9	38.0	0.099
1026	116.	*****	33.9	37.0	0.101
1031	121.	*****	33.9	37.0	0.096
1036	126.	*****	33.9	37.0	0.096
1041	131.	*****	33.9	37.5	0.099
1046	136.	*****	34.1	37.5	0.098
1051	141.	*****	33.9	37.0	0.098
1056	146.	*****	33.9	37.0	0.095
1101	151.	*****	34.1	37.5	0.094
1106	156.	*****	34.2	37.0	0.095
1111	161.	*****	34.2	37.0	0.093
1116	166.	*****	34.2	36.0	0.096
1121	171.	*****	34.2	36.0	0.093
1126	176.	*****	34.2	36.5	0.094
1131	181.	*****	34.2	36.5	0.094
1136	186.	*****	34.2	36.0	0.090
1141	191.	*****	34.3	35.0	0.094
1146	196.	*****	34.3	35.0	0.090
1151	201.	*****	34.3	34.0	0.089
1156	206.	*****	34.3	34.0	0.089
1201	211.	*****	34.3	33.5	0.092
1206	216.	*****	34.3	33.0	0.087
1211	221.	*****	34.5	33.0	0.089
1216	226.	*****	34.5	32.0	0.089

1221	231.	*****	34.5	32.5	0.089
1226	236.	*****	34.5	31.5	0.087
1231	241.	*****	34.5	31.0	0.084
1236	246.	*****	34.5	30.5	0.087

***** NO DATA TAKEN ----- DATA DISCARDED ----- 2 QUESTIONABLE DATA

AGC-218-14 SO2 40% RH
GLASS CHAMBER
1976 AUG 6

ADD 1410 MIN TO ELAPSED TIME
AT 1424 1 ML OF SO2 AND 1.6 ML OF PROPENE WERE INJECTED
CLIMET AND WHITBY WERE ON THE CHAMBER FROM 1313 TO 1645
DASIBI 1212 WAS ON THE CHAMBER FROM 1634 TO 1638

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
1241	251.	*****	34.9	32.0	0.085
1246	256.	*****	34.9	32.0	0.084
1251	261.	*****	34.9	31.5	0.087
1256	266.	*****	34.7	32.5	0.092
1301	271.	*****	34.7	32.5	0.093
1306	276.	*****	34.6	31.5	0.083
1311	281.	*****	34.6	31.5	0.083
1316	286.	*****	34.6	31.0	0.083
1321	291.	*****	34.5	30.5	0.081
1326	296.	*****	34.5	31.5	0.082
1331	301.	*****	34.5	31.5	0.082
1336	306.	*****	34.5	31.5	0.078
1341	311.	*****	34.6	29.5	0.078
1346	316.	*****	34.6	29.5	0.077
1351	321.	*****	34.5	30.0	0.073
1356	326.	*****	34.5	29.0	0.073
1401	331.	*****	34.6	29.0	0.073
1406	336.	*****	34.6	29.5	0.073
1411	341.	*****	34.6	30.0	0.072
1416	346.	*****	34.7	30.5	0.071
1421	351.	*****	34.6	31.0	0.073
1426	356.	*****	33.1	31.0	0.138
1431	361.	*****	34.3	31.0	0.221
1436	366.	*****	34.5	32.0	0.232
1441	371.	*****	34.6	33.5	0.231
1446	376.	*****	34.6	33.5	0.228
1451	381.	*****	34.7	34.0	0.226
1456	386.	*****	34.7	34.0	0.223
1501	391.	*****	34.7	34.5	0.222
1506	396.	*****	34.7	34.5	0.221
1511	401.	*****	34.7	35.0	0.217
1516	406.	*****	34.7	35.0	0.214
1521	411.	*****	34.7	35.0	0.211
1526	416.	*****	34.9	34.0	0.209
1531	421.	*****	34.9	33.5	0.206
1536	426.	*****	34.9	33.5	0.202
1541	431.	*****	34.9	33.0	0.202
1546	436.	*****	34.9	32.5	0.202
1551	441.	*****	35.0	32.0	0.198
1556	446.	*****	34.9	32.0	0.195
1601	451.	*****	35.0	31.5	0.192
1606	456.	*****	35.0	31.0	0.194
1611	461.	*****	35.0	30.0	0.191
1616	466.	*****	35.0	29.5	0.186
1621	471.	*****	35.0	29.5	0.184
1626	476.	*****	35.0	31.0	0.184
1631	481.	*****	35.0	31.5	0.181
1636	486.	0.407	35.1	32.5	0.180
1641	491.	*****	35.0	32.0	0.177
1646	496.	*****	35.1	33.5	0.181

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

ACC-219-1 SO2 80% RH
GLASS CHAMBER
1976 AUG 16

DARK

AT 1545 FC-12 WAS INJECTED INTO THE CHAMBER

AT 1646 SO2 WAS INJECTED INTO THE CHAMBER

TECO 43 SPANNED BASED ON CHAMBER INJECTION

TECO 43 SAMPLING RATE 1233 ML/MIN

BRADY 1296, CALIBRATION 1976 JUL 16

SO2 CORRECTION -0.1184 PPM

CLOCK TIME	ELAPSED TIME (MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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1733	3.	*****	*****	*****
1735	5.	32.6	81.5	0.237
1740	10.	32.6	81.5	0.290
1745	15.	32.8	81.5	0.296
1750	20.	32.6	81.5	0.297
1755	25.	32.6	81.5	0.302
1800	30.	32.7	81.0	0.306
1805	35.	32.7	81.0	0.303
1810	40.	32.7	81.0	0.307
1815	45.	32.3	81.0	0.303
1820	50.	32.7	81.0	0.304
1825	55.	32.7	81.0	0.304
1830	60.	33.0	80.5	0.302
1835	65.	32.8	80.5	0.302
1840	70.	32.7	80.5	0.302
1845	75.	33.0	80.5	0.299
1850	80.	32.7	80.5	0.303
1855	85.	32.7	80.5	0.297
1900	90.	32.8	80.5	0.297
1905	95.	33.2	80.5	0.292
1910	100.	33.2	80.5	0.292
1915	105.	33.1	80.5	0.292
1920	110.	33.1	80.5	0.290
1925	115.	33.1	80.5	0.237
1930	120.	33.1	80.5	0.293
1935	125.	33.1	80.5	0.295
1940	130.	33.1	80.5	0.233
1945	135.	33.0	80.5	0.282
1950	140.	33.0	80.5	0.281
1955	145.	33.0	80.5	0.281
2000	150.	32.8	80.5	0.232
2005	155.	33.0	80.5	0.280
2010	160.	33.0	80.5	0.276
2015	165.	32.8	80.5	0.275
2020	170.	32.8	80.5	0.272
2025	175.	33.0	80.5	0.266
2030	180.	32.8	80.5	0.272
2035	185.	33.4	79.5	0.263
2040	190.	33.5	79.0	0.269
2045	195.	33.5	78.5	0.259
2050	200.	33.8	77.0	0.253
2055	205.	33.8	77.0	0.260
2100	210.	33.8	76.5	0.254
2105	215.	33.9	76.5	0.258
2110	220.	33.9	76.5	0.257
2115	225.	33.9	76.5	0.258

2120	230.	34.2	76.0	0.253
2125	235.	34.2	76.0	0.250
2130	240.	34.1	76.0	0.250
2135	245.	34.3	76.0	0.247

***** NO DATA TAKEN

----- DATA DISCARDED

? QUESTIONABLE DATA

AGC-219-2 SO2 BD4 RH
GLASS CHAMBER
1976 AUG 16-17

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
2140	250.	34.2	76.0	0.250
2145	255.	33.9	76.0	0.247
2150	260.	33.8	76.0	0.244
2155	265.	33.8	76.0	0.244
2200	270.	33.9	75.5	0.239
2205	275.	33.8	75.5	0.247
2210	280.	33.7	75.5	0.243
2215	285.	33.9	75.5	0.241
2220	290.	33.8	75.5	0.241
2225	295.	33.7	75.5	0.239
2230	300.	33.9	75.5	0.234
2235	305.	33.8	75.5	0.235
2240	310.	33.7	75.5	0.236
2245	315.	33.9	75.5	0.235
2250	320.	33.7	75.5	0.235
2255	325.	33.7	75.5	0.231
2300	330.	33.8	75.5	0.231
2305	335.	33.7	75.5	0.228
2310	340.	33.7	75.5	0.225
2315	345.	33.7	75.5	0.224
2320	350.	33.5	75.5	0.221
2325	355.	33.5	75.5	0.225
2330	360.	33.7	75.5	0.226
2335	365.	33.5	75.5	0.220
2340	370.	33.5	75.5	0.219
2345	375.	33.5	75.5	0.224
2350	380.	33.4	75.5	0.221
2355	385.	33.4	75.5	0.220
0	390.	33.5	75.5	0.213
5	395.	33.4	75.5	0.216
10	400.	33.2	75.5	0.211
15	405.	33.4	75.5	0.213
20	410.	33.4	75.5	0.211
25	415.	33.2	75.5	0.214
30	420.	33.4	75.5	0.209
35	425.	33.2	75.5	0.214
40	430.	33.1	75.5	0.211
45	435.	33.2	75.5	0.206
50	440.	33.2	75.5	0.206
55	445.	33.1	75.5	0.205
100	450.	33.2	75.5	0.204
105	455.	33.1	75.5	0.204
110	460.	33.1	75.5	0.203
115	465.	33.2	75.5	0.197
120	470.	33.1	75.5	0.199
125	475.	33.1	75.5	0.200

130	480.	33.1	75.5	0.202
135	485.	33.0	75.5	0.195
140	490.	33.1	75.5	0.197
145	495.	33.1	75.5	0.193

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-219-3 SO2 80% RH
GLASS CHAMBER
1976 AUG 17

CLOCK TIME	ELAPSED TIME (MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
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150	500.	33.1	75.5	0.194
155	505.	33.1	75.5	0.192
200	510.	33.1	75.5	0.191
205	515.	33.0	75.5	0.187
210	520.	33.0	75.5	0.192
215	525.	33.1	75.5	0.184
220	530.	32.8	75.5	0.186
225	535.	33.0	75.0	0.187
230	540.	33.1	75.0	0.187
235	545.	32.8	75.5	0.182
240	550.	32.8	75.0	0.183
245	555.	33.0	75.0	0.182
250	560.	32.8	75.0	0.180
255	565.	32.8	75.0	0.179
300	570.	32.8	75.0	0.180
305	575.	32.7	75.0	0.178
310	580.	32.7	75.0	0.176
315	585.	33.0	75.0	0.175
320	590.	32.7	75.0	0.172
325	595.	32.7	75.0	0.173
330	600.	32.8	75.0	0.172
335	605.	32.7	75.0	0.175
340	610.	32.7	75.0	0.171
345	615.	32.8	75.0	0.170
350	620.	32.7	75.0	0.166
355	625.	32.7	75.0	0.169
400	630.	32.8	75.0	0.165
405	635.	32.7	75.0	0.165
410	640.	32.7	75.0	0.161
415	645.	32.8	75.0	0.162
420	650.	32.7	74.5	0.160
425	655.	32.7	74.5	0.158
430	660.	32.8	74.5	0.158
435	665.	32.7	74.5	0.159
440	670.	32.7	74.5	0.155
445	675.	32.8	75.0	0.158
450	680.	32.7	74.5	0.153
455	685.	32.7	74.5	0.153
500	690.	32.7	74.5	0.156
505	695.	32.7	74.5	0.150
510	700.	32.7	74.5	0.155
515	705.	32.7	74.5	0.152

***** NO DATA TAKEN

----- DATA DISCARDED

? QUESTIONABLE DATA

ADD 710 MIN TO ELAPSED TIME

520	0.	32.6	74.5	0.149
525	5.	32.6	74.5	0.150
530	10.	32.7	74.5	0.147
535	15.	32.6	74.5	0.148
540	20.	32.6	74.5	0.147
545	25.	32.7	74.5	0.143
550	30.	32.4	74.5	0.144
555	35.	32.6	74.5	0.143
600	40.	32.6	74.5	0.142
605	45.	32.4	74.5	0.138
610	50.	32.4	74.5	0.138
615	55.	32.7	74.5	0.139
620	60.	32.4	74.5	0.142
625	65.	32.4	74.5	0.136
630	70.	32.6	74.5	0.134
635	75.	32.4	74.5	0.133
640	80.	32.4	74.0	0.136
645	85.	32.4	74.0	0.132
650	90.	32.4	74.0	0.131
655	95.	32.4	74.0	0.131
700	100.	32.6	74.0	0.131
705	105.	32.4	74.0	0.127
710	110.	32.4	74.0	0.128
715	115.	32.6	74.0	0.127
720	120.	32.8	73.5	0.126
725	125.	33.0	73.0	0.127
730	130.	33.2	72.5	0.128
735	135.	33.2	72.0	0.121
740	140.	33.4	72.0	0.125
745	145.	33.5	71.5	0.122
750	150.	33.4	71.5	0.121
755	155.	33.4	71.5	0.122
800	160.	33.7	71.5	0.122
805	165.	33.2	72.0	0.121
810	170.	33.1	72.0	0.119
815	175.	33.0	72.0	0.119
820	180.	33.0	72.0	0.122
825	185.	33.0	72.0	0.119
830	190.	33.0	72.0	0.115
835	195.	32.8	72.0	0.120
840	200.	32.8	72.0	0.112
845	205.	32.8	72.0	0.119
850	210.	32.8	72.0	0.112
855	215.	32.8	72.0	0.114
900	220.	33.0	72.0	0.110
905	225.	32.8	72.0	0.110

***** NO DATA TAKEN

--- DATA DISCARDED

7 QUESTIONABLE DATA

AGC-219-5 SO2 80% RH
GLASS CHAMBER
1976 AUG 17

ADD 710 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
930	250.	32.8	74.0	0.103
935	255.	32.7	74.0	0.104
940	260.	32.7	74.0	0.104
945	265.	32.8	74.0	0.106
950	270.	32.7	73.5	0.108
955	275.	32.8	73.0	0.105
1000	280.	32.7	73.0	0.106

***** NO DATA TAKEN ----- DATA DISCARDED ? QUESTIONABLE DATA

AGC-220-1 SO2-O3 PROPENE
GLASS CHAMBER
1976 AUG 19

DARK
SO2 AND FC-12 INJECTED AT 1115
OZONE ADDED AT 1149, PROPENE AT 1155
BRADY 1296, CALIBRATION 1976 JULY 16

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)	PROPENE (PPM)
1200	0.	0.664	32.7	41.0	0.363	1.014
1205	5.	0.606	32.8	41.0	0.344	*****
1211	11.	0.557	32.8	41.0	0.331	*****
1216	16.	0.511	32.8	41.0	0.318	0.801
1221	21.	0.474	32.7	41.0	0.304	*****
1226	26.	0.440	32.7	41.0	0.297	*****
1230	30.	0.420	32.8	41.0	0.291	0.683
1235	35.	0.393	32.7	41.0	0.283	*****
1240	40.	0.371	32.8	41.0	0.276	*****
1245	45.	0.352	32.6	41.0	0.271	0.593
1250	50.	0.335	32.6	41.0	0.266	*****
1255	55.	0.318	33.0	40.5	0.266	*****
1300	60.	0.303	33.0	40.5	0.260	0.522
1305	65.	0.286	32.8	40.5	0.258	*****
1310	70.	0.274	32.8	40.5	0.254	*****
1315	75.	0.259	32.8	40.5	0.250	*****
1320	80.	0.249	32.8	40.5	0.246	*****
1325	85.	0.239	32.8	40.5	0.249	*****
1331	91.	0.230	32.8	40.0	0.247	0.434
1336	96.	0.222	32.8	40.0	0.244	*****
1341	101.	0.213	32.8	40.0	0.242	*****
1346	106.	0.205	32.8	40.0	0.238	*****
1350	110.	0.200	32.8	40.0	0.239	*****
1355	115.	0.191	32.8	40.0	0.239	*****
1400	120.	0.186	33.0	39.5	0.237	0.376
1405	125.	0.178	32.8	39.5	0.236	*****
1410	130.	0.176	32.8	39.5	0.233	*****
1415	135.	0.166	32.8	39.5	0.231	*****
1420	140.	0.161	32.8	39.5	0.232	*****
1425	145.	0.159	32.8	39.5	0.230	*****
1430	150.	0.151	32.8	39.5	0.230	0.336
1435	155.	0.147	33.0	39.5	0.226	*****
1440	160.	0.142	32.8	39.5	0.225	*****
1445	165.	0.139	33.0	39.5	0.225	*****
1451	171.	0.134	32.8	39.5	0.223	*****
1456	176.	0.122	32.8	39.5	0.223	*****
1501	181.	0.127	32.8	39.0	0.222	0.311
1506	186.	0.122	32.8	39.0	0.225	*****
1510	190.	0.122	33.0	39.0	0.221	*****
1515	195.	0.120	32.8	39.0	0.221	*****
1520	200.	0.115	32.8	39.0	0.220	*****
1525	205.	0.110	32.8	39.0	0.220	*****
1530	210.	0.110	33.0	39.0	0.221	0.289
1535	215.	0.105	32.8	39.0	0.216	*****
1540	220.	*****	32.8	39.0	0.216	*****
1545	225.	*****	32.8	39.0	0.215	*****

1550	230.	*****	32.8	39.0	0.215	*****
1555	235.	*****	33.0	39.0	0.215	*****
1600	240.	*****	33.0	39.0	0.213	0.274
1605	245.	0.088	32.8	39.0	0.211	*****

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

AGC-220-2 SO2-O3 PROPENE
GLASS CHAMBER
1976 AUG 19

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)	PROPENE (PPM)
1611	251.	0.085	33.0	38.5	0.214	*****
1616	256.	0.090	32.8	38.5	0.211	*****
1621	261.	0.085	33.0	38.5	0.211	*****
1626	266.	0.083	33.0	38.5	0.208	*****
1630	270.	0.083	33.0	38.5	0.209	0.254
1635	275.	0.081	33.0	38.5	0.208	*****
1640	280.	0.078	33.0	38.5	0.209	*****
1645	285.	0.076	33.1	38.5	0.205	*****
1650	290.	0.076	33.0	38.5	0.205	*****
1655	295.	0.076	33.0	38.5	0.206	*****
1700	300.	0.071	33.8	38.5	0.205	0.248

***** NO DATA TAKEN --- DATA DISCARDED ? QUESTIONABLE DATA

AGC-221-1 S02-03
GLASS CHAMBER
1976 AUG 20

DARK
BRADY 1296, CALIBRATION 1976 JULY 16
OZONE WAS INJECTED AT 0933

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
845	0.	0.0	32.7	44.0	0.379
850	5.	0.0	33.0	43.5	0.380
855	10.	0.0	33.0	43.5	0.377
900	15.	0.0	33.1	43.5	0.376
905	20.	0.0	33.0	43.5	0.376
910	25.	0.0	33.0	43.5	0.370
915	30.	0.0	33.1	43.0	0.370
920	35.	0.0	33.0	43.0	0.369
925	40.	0.0	33.1	43.0	0.369
930	45.	0.0	33.0	43.0	0.366
935	50.	0.572	32.4	42.5	0.360
940	55.	0.576	33.0	42.5	0.358
946	61.	0.572	33.0	42.5	0.357
951	66.	0.572	33.0	42.5	0.355
956	71.	0.569	33.0	42.5	0.352
1000	75.	0.567	33.0	42.5	0.352
1005	80.	0.567	33.0	42.5	0.349
1010	85.	0.562	33.0	42.5	0.349
1015	90.	0.556	33.0	42.0	0.347
1020	95.	0.557	33.0	42.0	0.347
1025	100.	0.554	33.1	42.0	0.344
1030	105.	0.552	33.0	42.0	0.346
1035	110.	0.552	33.0	42.0	0.342
1040	115.	0.550	33.0	42.0	0.340
1045	120.	0.545	33.0	42.0	0.342
1050	125.	0.542	33.1	42.0	0.340
1055	130.	0.542	33.1	41.5	0.340
1100	135.	0.540	33.1	41.5	0.340
1106	141.	0.537	33.0	41.5	0.336
1111	146.	0.537	33.1	41.5	0.335
1116	151.	0.532	33.0	41.5	0.333
1120	155.	0.532	33.1	41.5	0.335
1125	160.	0.530	33.1	41.5	0.333
1130	165.	0.530	33.1	41.0	0.332
1135	170.	0.528	33.0	41.0	0.331
1140	175.	0.528	33.0	41.0	0.330
1145	180.	0.523	33.0	41.0	0.329
1150	185.	0.520	33.0	41.0	0.326
1155	190.	0.520	33.0	41.0	0.325
1200	195.	0.515	33.0	41.0	0.321
1205	200.	0.518	33.1	40.5	0.324
1210	205.	0.513	33.0	40.5	0.321
1215	210.	0.511	33.0	40.5	0.319
1220	215.	*****	33.1	40.5	0.320
1226	221.	0.508	33.0	40.5	0.319
1231	226.	0.508	33.1	40.5	0.319

1236	231.	0.503	33.0	40.5	0.319
1240	235.	0.501	33.0	40.5	0.318
1245	240.	0.501	33.0	40.0	0.315
1250	245.	0.498	33.0	40.0	0.314

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-221-2 S02-03
GLASS CHAMBER
1976 AUG 20

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	TSE (DEG C)	REL HUM (%)	S02 (PPM)
1255	250.	0.498	33.0	40.0	0.313
1300	255.	0.493	33.1	40.0	0.313
1305	260.	0.493	33.0	40.0	0.309
1310	265.	0.491	33.0	39.5	0.308
1315	270.	0.491	33.2	39.5	0.308
1320	275.	0.489	33.1	39.5	0.310
1325	280.	0.489	33.1	39.0	0.309
1330	285.	0.484	33.2	39.0	0.307
1335	290.	0.484	33.2	39.0	0.308
1340	295.	0.481	33.2	39.0	0.304
1346	301.	0.481	33.2	38.5	0.303
1351	306.	0.479	33.2	39.0	0.304
1356	311.	0.479	33.1	39.0	0.303
1400	315.	0.476	33.1	39.0	0.302
1405	320.	0.476	33.1	39.0	0.299
1410	325.	0.474	33.1	39.0	0.298
1415	330.	0.474	33.1	38.5	0.298
1420	335.	0.471	33.1	38.5	0.296
1425	340.	0.469	33.1	38.5	0.294
1430	345.	0.467	33.2	38.5	0.296

***** NO DATA TAKEN

--- DATA DISCARDED

? QUESTIONABLE DATA

ACC-222-1 SJ2-NOX-SURR-U
GLASS CHAMBER
1976 AUG 24

DARK
CO FACTOR 1.9/1.22: BRADY 1295
2.1 ML NOX INJECTED AT 0920 HOURS
AT T=0: NON-METHANE HC = 1740 PPSC; METHANE = 3200 PPB

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	CO (PPM)	TSI (DEG C)	REL HUM (%)	SO2 (PPM)
945	0.	0.0	5.63	33.2	46.5	0.349
950	5.	0.0	5.60	33.1	46.5	0.348
955	10.	0.002	5.65	33.1	46.5	0.344
1000	15.	0.0	5.61	33.0	46.5	0.344
1005	20.	0.0	5.60	33.0	46.5	0.340
1010	25.	*****	*****	*****	*****	*****
1015	30.	0.0	5.63	33.0	46.5	0.338
1020	35.	0.0	5.64	33.0	46.5	0.338
1025	40.	0.0	5.58	33.0	46.5	0.337
1030	45.	0.0	5.58	33.0	46.5	0.333
1035	50.	0.0	5.56	33.0	46.5	0.335
1040	55.	0.0	5.56	33.0	46.0	0.332
1045	60.	0.0	5.51	33.0	46.0	0.332
1050	65.	0.0	5.52	33.0	46.0	0.333
1055	70.	0.0	5.48	33.0	46.0	0.329
1100	75.	0.0	5.48	33.0	45.5	0.329
1105	80.	0.0	5.48	33.0	45.5	0.327
1110	85.	0.0	5.47	33.1	45.5	0.326
1115	90.	0.0	5.50	33.1	45.5	0.326
1120	95.	0.0	5.48	33.1	45.5	0.325
1125	100.	0.0	5.45	33.1	45.5	0.324
1130	105.	0.002	5.42	33.0	45.0	0.322
1135	110.	0.0	5.40	33.0	45.0	0.319
1140	115.	0.002	5.42	33.0	45.0	0.320
1145	120.	0.002	5.38	33.0	45.0	0.319
1150	125.	0.0	5.40	33.0	45.0	0.318
1155	131.	0.0	5.41	33.0	45.0	0.318
1200	135.	0.0	5.32	33.0	45.0	0.314
1205	140.	0.010	5.39	33.0	45.0	0.311
1210	145.	0.0	5.35	33.0	45.0	0.314
1215	150.	0.0	5.34	32.8	45.0	0.313
1220	155.	0.0	5.33	33.0	44.5	0.310
1225	160.	0.0	5.34	33.0	44.5	0.313
1230	165.	0.0	5.26	33.0	44.5	0.313
1235	170.	0.0	5.31	33.0	44.5	0.310
1240	175.	0.0	5.30	33.2	44.0	0.308
1245	180.	0.0	5.26	33.1	44.0	0.308
1250	185.	0.0	5.28	33.2	44.0	0.307
1255	190.	0.0	5.29	33.2	43.5	0.304
1300	195.	0.0	5.29	33.2	43.5	0.305
1305	200.	0.0	5.26	33.2	43.5	0.304
1310	205.	0.0	5.24	33.2	43.5	0.304
1315	210.	0.002	5.24	33.2	43.5	0.302
1320	215.	0.0	5.23	33.2	43.5	0.300
1325	220.	0.0	5.18	33.2	43.0	0.300
1330	225.	0.0	5.19	33.2	43.0	0.300

1335	230.	0.0	5.19	33.2	43.0	0.300
1341	236.	0.002	5.16	33.1	43.0	0.297
1345	240.	0.0	5.15	33.1	43.0	0.297
1350	245.	0.0	5.13	33.2	43.0	0.296

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-222-2 S02-NOX-SURR-U
GLASS CHAMBER
1976 AUG 24

SPECIAL Moore Business Forms, Inc.

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	CO (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
1355	250.	0.0	5.13	33.2	43.C	0.296
1400	255.	0.0	5.12	33.2	43.C	0.294
1405	260.	0.0	5.12	33.2	43.C	0.293
1410	265.	0.0	5.12	33.0	43.C	0.291
1415	270.	0.0	5.06	33.0	43.0	0.291
1420	275.	0.0	5.07	32.8	43.0	0.291
1425	280.	0.0	5.03	32.8	43.C	0.291
1430	285.	0.0	5.78	32.8	42.5	0.291
1435	290.	0.0	5.04	32.8	42.5	0.291
1440	295.	0.0	5.04	33.0	42.5	0.289
1445	300.	0.0	5.02	33.0	42.5	0.283
1450	305.	0.0	5.02	33.0	42.5	0.288
1455	310.	0.0	4.97	33.0	42.0	0.283
1500	315.	0.0	4.99	33.0	42.0	0.285
1505	320.	0.0	4.96	33.0	42.C	0.285
1510	325.	0.0	5.00	33.0	42.0	0.285
1515	330.	0.0	5.01	33.0	42.0	0.285
1520	335.	0.002	4.93	33.0	41.5	0.282
1526	341.	0.0	4.96	33.1	41.5	0.281
1530	345.	0.0	4.93	33.4	41.5	0.280
1535	350.	0.0	4.92	33.2	41.5	0.280
1540	355.	0.002	4.91	33.1	41.5	0.278
1545	360.	0.002	4.92	33.0	41.5	0.280
1550	365.	0.0	4.93	32.8	41.5	0.276
1555	370.	0.0	4.89	32.8	41.5	0.276
1600	375.	0.0	4.89	32.8	41.5	0.275
1605	380.	0.0	4.88	33.0	41.5	0.271
1610	385.	0.002	4.90	32.8	41.0	0.274
1615	390.	0.002	4.83	33.0	41.0	0.272
1620	395.	0.0	4.87	33.0	41.0	0.271
1625	400.	0.0	4.81	33.0	41.0	0.274
1630	405.	0.002	4.81	33.0	41.0	0.270
1635	410.	0.002	4.87	33.0	41.0	0.270
1640	415.	0.0	4.80	33.0	40.5	0.270
1645	420.	0.002	4.85	33.0	40.5	0.269
1650	425.	0.002	4.81	33.0	40.5	0.270
1655	430.	0.0	4.83	33.0	40.5	0.266
1700	435.	0.0	4.84	33.0	40.5	0.265
1705	440.	0.0	4.82	33.0	40.5	0.266
1711	446.	0.0	4.82	33.1	40.5	0.266
1715	450.	0.0	4.77	33.2	40.C	0.264
1720	455.	0.0	4.74	33.2	40.C	0.264
1725	460.	0.0	4.79	33.2	40.C	0.265
1730	465.	0.0	4.79	33.2	40.C	0.265
1735	470.	0.0	4.80	33.1	40.0	0.264
1740	475.	0.0	4.75	33.2	40.C	0.265

1745	480.	0.0	4.80	33.2	40.C	0.265
1750	485.	0.0	4.77	33.2	40.C	0.261
1755	490.	0.0	4.72	33.2	40.C	0.260
1800	495.	0.0	4.72	33.1	40.0	0.260

***** NO DATA TAKEN ----- DATA DISCARDED ? QUESTIONABLE DATA

AGC-222-3 SO2-NOX-SURR-U
GLASS CHAMBER
1976 AUG 24

MOORE BUSINESS FORMS, INC.

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	CO (PPM)	TSI (DEG C)	REL HUM (%)	SO2 (PPM)
1805	500.	0.0	4.72	33.1	39.5	0.261
1810	505.	0.0	4.72	33.2	39.5	0.256
1815	510.	0.0	4.70	33.9	39.5	0.259
1820	515.	0.0	4.69	34.1	39.5	0.256
1825	520.	0.0	4.69	34.1	39.5	0.256
1830	525.	0.0	4.68	34.1	39.5	0.255
1835	530.	0.0	4.67	34.1	39.5	0.256
1840	535.	0.0	4.66	34.2	39.5	0.254
1845	540.	0.0	4.69	34.2	39.5	0.254
1850	545.	0.0	4.67	34.2	39.5	0.253
1856	551.	0.0	4.66	34.3	39.5	0.255
1900	555.	0.0	4.66	34.1	39.5	0.254
1905	560.	0.0	4.70	34.1	39.5	0.254
1910	565.	0.0	4.65	34.1	39.5	0.252
1915	570.	0.0	4.61	34.1	39.5	0.252
1920	575.	0.0	4.64	34.1	39.5	0.249
1925	580.	0.0	4.58	34.1	39.0	0.249
1930	585.	0.0	4.58	34.1	39.0	0.247
1935	590.	0.0	4.65	34.1	39.5	0.249
1940	595.	0.0	4.60	33.9	39.0	0.245
1945	600.	0.0	4.58	33.9	39.0	0.245
1950	605.	0.0	4.58	34.1	39.0	0.247
1955	610.	0.0	4.61	33.8	39.0	0.244
2000	615.	0.0	4.60	33.8	39.0	0.245
2005	620.	0.0	4.56	33.9	39.0	0.244
2010	625.	0.0	4.54	33.9	39.0	0.245
2015	630.	0.002	4.59	33.9	39.0	0.243
2020	635.	0.0	4.56	33.9	39.0	0.245
2025	640.	0.002	4.53	33.9	39.0	0.241
2030	645.	0.0	4.55	33.9	39.0	0.241
2035	650.	0.0	4.58	33.9	39.0	0.239
2041	656.	0.002	4.59	33.9	39.0	0.239
2045	660.	0.002	4.59	33.8	38.5	0.238
2050	665.	0.002	4.52	33.8	38.5	0.237
2055	670.	0.0	4.51	33.9	38.5	0.237
2100	675.	0.0	4.51	33.9	38.5	0.237
2105	680.	0.0	4.48	33.9	38.5	0.237
2110	685.	0.0	4.53	33.9	38.5	0.236
2115	690.	0.0	4.48	33.9	38.5	0.236
2120	695.	0.0	4.49	33.9	38.5	0.236
2125	700.	0.0	4.55	33.9	38.5	0.232
2130	705.	0.0	4.49	33.9	38.5	0.234

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

AGC-222-A SO2-NOX-SURR-G
GLASS CHAMBER
1976 AUG 24-25

ADD 710 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	CO (PPM)	TSI (DEG C)	REF HUM (%)	SO2 (PPM)
2135	0.	0.0	4.48	33.9	38.5	0.232
2140	5.	0.0	4.51	33.8	38.5	0.232
2145	10.	0.0	4.46	33.8	38.5	0.231
2150	15.	0.0	4.48	33.9	38.5	0.231
2155	20.	0.0	4.45	33.9	38.5	0.231
2200	25.	0.0	4.46	33.9	38.5	0.228
2205	30.	0.0	4.46	33.8	38.5	0.228
2210	35.	0.0	4.40	33.9	38.5	0.227
2215	40.	0.0	4.41	33.8	38.5	0.228
2220	45.	0.0	4.40	33.8	38.5	0.230
2226	51.	0.0	4.43	33.8	38.5	0.227
2230	55.	0.0	4.43	33.7	38.5	0.230
2235	60.	0.0	4.42	33.7	38.5	0.225
2240	65.	0.0	4.40	33.7	38.5	0.228
2245	70.	0.0	4.37	33.8	38.5	0.226
2250	75.	0.0	4.42	33.7	38.5	0.223
2255	80.	0.0	4.43	33.5	38.5	0.223
2300	85.	0.0	4.43	33.5	38.5	0.223
2305	90.	0.0	4.43	33.5	38.5	0.222
2310	95.	0.0	4.40	33.4	38.5	0.221
2315	100.	0.0	4.36	33.4	38.5	0.221
2320	105.	0.0	4.39	33.4	38.5	0.221
2325	110.	0.0	4.40	33.2	38.5	0.222
2330	115.	0.0	4.41	33.2	38.5	0.221
2335	120.	0.0	4.30	33.2	38.5	0.220
2340	125.	0.0	4.34	33.2	38.5	0.223
2345	130.	0.0	4.33	33.2	38.5	0.222
2350	135.	0.0	4.34	33.1	38.5	0.219
2355	140.	0.0	4.36	33.1	38.5	0.217
0	145.	0.0	4.32	33.1	38.5	0.219
5	150.	0.0	4.31	33.1	38.5	0.220
11	156.	0.0	4.27	33.0	38.5	0.216
15	160.	0.0	4.27	32.8	39.0	0.216
20	165.	0.0	4.29	32.8	39.0	0.216
25	170.	0.0	4.28	32.8	39.0	0.215
30	175.	0.0	4.23	33.0	39.0	0.215
35	180.	0.0	4.24	32.8	39.0	0.214
40	185.	0.0	4.29	32.8	39.0	0.217
45	190.	0.0	4.25	32.8	39.0	0.213
50	195.	0.0	4.31	32.8	39.0	0.213
55	200.	0.0	4.25	32.8	39.0	0.211
100	255.	0.0	4.27	32.8	39.0	0.214
105	210.	0.0	4.27	32.7	39.0	0.211
110	215.	0.0	4.26	32.6	39.0	0.211
115	220.	0.0	4.25	32.6	39.0	0.209
120	225.	0.0	4.23	32.7	39.0	0.213

125	230.	0.0	4.22	32.7	39.0	0.209
130	235.	0.0	4.21	32.7	39.0	0.210
135	240.	0.0	4.24	32.7	39.0	0.215
140	245.	0.0	4.25	32.7	39.0	0.208

***** NO DATA TAKEN

----- DATA DISCARDED

? QUESTIONABLE DATA

AGC-222-5 SC2-NOX-SURR-U
GLASS CHAMBER
1976 AUG 25

ADD 710 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	CO (PPM)	ISL (DEG C)	REL HUM (%)	SO2 (PPM)
145	250.	0.0	4.15	32.4	39.0	0.203
150	255.	0.0	4.21	32.6	39.0	0.204
155	261.	0.0	4.21	32.6	39.0	0.208
200	265.	0.0	4.19	32.4	39.0	0.205
205	270.	0.0	4.22	32.3	39.0	0.209
210	275.	0.0	4.23	32.4	39.0	0.202
215	280.	0.0	4.16	32.4	39.0	0.204
220	285.	0.0	4.19	32.3	39.0	0.205
225	290.	0.0	4.16	32.3	39.5	0.206
230	295.	0.0	4.17	32.3	39.5	0.205
235	300.	0.0	4.16	32.3	39.5	0.207
240	305.	0.0	4.16	32.3	39.5	0.202
245	310.	0.0	4.21	32.3	39.5	0.205
250	315.	0.0	4.16	31.5	39.5	0.200
255	320.	0.0	4.11	31.6	39.5	0.202
300	325.	0.0	4.07	31.5	39.5	0.202
305	330.	0.0	4.14	31.3	39.5	0.205
310	335.	0.0	4.10	31.3	39.5	0.202
315	340.	0.0	4.13	31.3	39.5	0.200
320	345.	0.0	4.14	31.3	39.5	0.200
325	350.	0.0	4.09	31.3	39.5	0.198
330	355.	0.0	4.10	31.2	39.5	0.197
335	360.	0.0	4.10	31.2	39.5	0.196
341	366.	0.0	4.04	31.2	39.5	0.197
345	370.	0.0	4.08	31.2	39.5	0.197
350	375.	0.0	4.08	31.2	39.5	0.190
355	380.	0.0	4.01	31.2	39.5	0.195
400	385.	0.0	4.02	31.2	39.5	0.195
405	390.	0.0	4.00	31.1	39.5	0.195
410	395.	0.0	4.04	31.2	39.5	0.197
415	400.	0.0	4.07	31.1	39.5	0.192
420	405.	0.0	4.04	31.1	39.5	0.192
425	410.	0.0	4.02	31.1	39.5	0.192
430	415.	0.0	3.99	31.1	39.5	0.195
435	420.	0.0	4.07	31.1	39.5	0.191
440	425.	0.0	4.02	31.1	39.5	0.189
445	430.	0.0	3.98	31.1	39.5	0.189
450	435.	0.0	3.93	31.1	39.5	0.189
455	440.	0.0	4.00	31.1	39.5	0.186
500	445.	0.0	4.01	30.8	39.5	0.186
505	450.	0.0	4.00	30.9	39.5	0.186
510	455.	0.0	3.95	30.9	39.5	0.185
515	460.	0.0	3.98	30.9	39.5	0.187
520	465.	0.0	3.97	30.8	39.5	0.186
526	471.	0.0	3.95	30.8	39.5	0.187
530	475.	0.0	4.01	30.8	39.5	0.186

535	480.	0.0	3.92	30.8	39.5	0.187
540	485.	0.0	4.00	30.8	39.5	0.184
545	490.	0.0	3.99	30.7	39.5	0.185
550	495.	0.0	3.96	30.8	39.5	0.184

***** NO DATA TAKEN

----- DATA DISCARDED

? UNRELIABLE DATA

AGC-222-6 S32-NOX-SURR-U
GLASS CHAMBER
1976 AUG 25

ADD 710 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME (MIN)	ZONE (PPM)	CO (PPM)	TS1 (DEG C)	REL HUM (%)	S32 (PPM)
555	500.	0.0	2.93	30.7	39.5	0.184
600	505.	0.0	3.93	30.7	39.5	0.182
605	510.	0.0	3.96	30.7	39.5	0.183
610	515.	0.0	3.98	30.7	39.5	0.182
615	520.	0.0	3.96	30.7	39.5	0.183
620	525.	0.0	3.97	30.7	39.5	0.184
625	530.	0.0	3.92	30.7	39.5	0.180
630	535.	0.0	3.89	30.7	39.5	0.180
635	540.	0.0	3.95	30.7	39.5	0.181
640	545.	0.002	3.92	30.7	39.5	0.178
645	550.	0.0	3.91	30.5	39.5	0.181
650	555.	0.0	3.88	30.5	39.5	0.173
655	560.	0.0	3.90	30.5	39.5	0.177
700	565.	0.0	3.89	30.5	39.5	0.177
705	570.	0.0	3.91	30.7	39.5	0.170
711	576.	0.0	3.91	30.5	39.5	0.177
715	580.	0.002	3.86	30.5	39.5	0.176
720	585.	0.0	3.86	30.5	39.0	0.173
725	590.	0.0	3.91	30.5	39.0	0.177
730	595.	0.002	3.86	30.5	39.0	0.176
735	600.	0.002	3.82	30.5	39.0	0.176
740	605.	0.002	3.87	30.5	39.0	0.175
745	610.	0.0	3.81	30.5	39.0	0.173
750	615.	0.0	3.81	30.9	39.0	0.172
755	620.	0.002	3.85	31.2	39.5	0.172
800	625.	0.0	3.81	31.3	39.0	0.172
805	630.	0.002	3.84	31.6	39.0	0.172
810	635.	0.0	3.83	31.8	39.5	0.172
815	640.	0.0	3.85	32.0	39.0	0.173
820	645.	0.0	3.82	32.0	39.0	0.172
825	650.	0.0	3.81	32.3	39.5	0.171
830	655.	0.0	3.86	32.3	39.5	0.170
835	660.	0.0	3.77	32.3	39.0	0.170
840	665.	0.0	3.80	32.4	39.0	0.169
845	670.	0.0	3.78	32.6	34.5	0.171
850	675.	0.0	3.86	32.7	34.9	0.169
855	681.	0.0	3.80	32.7	39.0	0.167
900	685.	0.0	3.78	32.8	34.0	0.167
905	690.	0.0	3.78	32.8	34.0	0.169
910	695.	0.0	3.84	32.8	34.0	0.169

***** NO DATA TAKEN ----- DATA DISCARDED ? QUESTIONABLE DATA

AGC-222-7 S02-NOX-SURR-U
GLASS CHAMBER
1976 AUG 25

ADD 710 MIN TO ELAPSED TIME

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	CO (PPM)	TS1 (DEG C)	REL HUM (%)	S02 (PPM)
915	700.	0.0	3.79	32.7	34.0	0.167
920	705.	0.002	3.77	32.7	34.0	0.169
925	710.	0.0	3.79	32.7	34.0	0.169
930	715.	0.0	3.79	32.7	33.5	0.162
935	720.	0.0	3.77	32.7	33.5	0.164
940	725.	0.0	3.77	32.8	33.5	0.162
945	730.	0.0	3.79	32.3	33.5	0.164
950	735.	0.0	3.73	32.8	33.0	0.162
955	740.	0.0	3.79	32.8	33.0	0.164
1000	745.	0.0	3.76	33.5	33.0	0.162
1005	750.	0.0	3.75	33.8	32.0	0.162
1010	755.	0.0	3.76	33.8	33.0	0.161
1015	760.	0.0	3.72	33.8	32.5	0.160
1020	765.	0.0	3.73	33.9	32.5	0.161
1025	770.	0.0	3.75	33.9	32.5	0.159
1030	775.	0.0	3.78	33.8	32.5	0.159
1035	780.	0.002	3.75	33.8	32.5	0.158
1041	785.	0.0	3.75	33.8	32.5	0.161
1045	790.	0.0	3.75	33.7	32.5	0.158
1050	795.	0.0	3.76	33.7	32.5	0.158
1055	800.	0.0	3.75	33.8	32.5	0.156

***** NO DATA TAKEN ---- DATA DISCARDED ? QUESTIONABLE DATA

AGC-222-B SO2-NOx-SURR-U

GLASS CHAMBER

1976 AUG 25

LIGHTS ON 1100; INTENSITY 100%

CO FACTOR 1.9/1.22; BRACY 1296

TECO 140 WAS ON THE CHAMBER FROM 1105 TO 1111, 1200 TO 1205, 1300 TO 1305, 1400 TO 1405, 1500 TO 1505, 1605 TO 1610, AND 1655 TO 1700

TECO 140 SAMPLING RATE: 1128 ML/MIN

PAN NOT MEASURED; NO2 AND NOx VALUES NOT CORRECTED

AT T=15 MIN: NON-METHANE HC = 1130 PPB; METHANE = 2960 PPB

CLOCK TIME	ELAPSED TIME(MIN)	OZONE (PPM)	NO (PPM)	NO2-PAN (PPM)	NOx-PAN (PPM)	CO (PPM)	TS1 (DEG C)	REL HUM (%)	SO2 (PPM)
1100	0.	0.0	*****	*****	*****	3.75	33.0	32.0	0.158
1105	5.	0.027	*****	*****	*****	3.74	33.8	32.0	0.154
1110	10.	0.054	0.030	0.500	0.530	3.74	34.1	31.5	0.153
1115	15.	0.076	*****	*****	*****	3.75	34.3	32.0	0.149
1120	20.	0.095	*****	*****	*****	3.73	34.3	32.5	0.149
1125	25.	0.110	*****	*****	*****	3.73	34.1	32.5	0.148
1130	30.	0.122	*****	*****	*****	3.73	34.1	32.5	0.145
1135	35.	0.132	*****	*****	*****	3.76	34.1	32.5	0.148
1140	40.	0.142	*****	*****	*****	3.73	34.1	32.5	0.147
1145	45.	0.154	*****	*****	*****	3.73	34.2	32.0	0.142
1150	50.	0.164	*****	*****	*****	3.73	34.3	32.0	0.143
1155	55.	0.176	*****	*****	*****	3.73	33.4	31.5	0.143
1200	60.	0.181	*****	*****	*****	3.72	33.5	31.5	0.144
1205	65.	0.188	0.021	0.449	0.468	3.71	33.5	31.5	0.140
1210	70.	0.198	*****	*****	*****	3.73	33.5	31.0	0.140
1215	75.	0.208	*****	*****	*****	3.69	33.7	31.0	0.138
1220	80.	0.217	*****	*****	*****	3.72	33.7	31.0	0.138
1226	86.	0.225	*****	*****	*****	3.71	33.8	30.5	0.138
1230	90.	0.227	*****	*****	*****	3.71	33.8	30.5	0.137
1235	95.	0.234	*****	*****	*****	3.73	33.9	30.5	0.138
1240	100.	0.244	*****	*****	*****	3.74	33.8	30.5	0.136
1245	105.	0.254	*****	*****	*****	3.66	33.9	30.5	0.136
1250	110.	0.259	*****	*****	*****	3.70	33.9	30.0	0.137
1255	115.	0.269	*****	*****	*****	3.69	33.9	30.0	0.136
1300	120.	0.264	*****	*****	*****	3.71	34.1	30.0	0.132
1305	125.	0.283	0.020	0.370	0.390	3.62	34.1	29.5	0.134
1310	130.	0.288	*****	*****	*****	3.68	34.3	29.5	0.133
1315	135.	0.298	*****	*****	*****	3.69	34.2	29.5	0.133
1320	140.	0.303	*****	*****	*****	3.67	34.3	29.5	0.131
1325	145.	0.313	*****	*****	*****	3.70	35.3	29.5	0.132
1330	150.	0.316	*****	*****	*****	3.65	35.3	29.0	0.129
1335	155.	0.325	*****	*****	*****	3.67	34.5	29.0	0.129
1340	160.	0.332	*****	*****	*****	3.70	35.6	29.0	0.129
1345	165.	0.337	*****	*****	*****	3.69	35.6	29.0	0.129
1350	170.	0.344	*****	*****	*****	3.60	35.6	28.5	0.129
1355	175.	0.352	*****	*****	*****	3.65	35.7	28.5	0.129
1400	180.	0.357	*****	*****	*****	3.65	35.7	28.5	0.126
1405	185.	0.362	0.025	0.310	0.335	3.67	35.7	28.5	0.127
1411	191.	0.371	*****	*****	*****	3.64	35.7	28.0	0.125
1415	195.	0.376	*****	*****	*****	3.64	35.7	28.5	0.125
1420	200.	0.383	*****	*****	*****	3.64	35.7	28.0	0.123
1425	205.	0.391	*****	*****	*****	3.61	35.8	28.0	0.125
1430	210.	0.396	*****	*****	*****	3.58	36.0	28.0	0.125
1435	215.	0.401	*****	*****	*****	3.62	36.0	28.0	0.122
1440	220.	0.410	*****	*****	*****	3.62	34.9	28.0	0.122
1445	225.	0.413	*****	*****	*****	3.62	35.0	28.0	0.122

1450	230.	0.423	*****	*****	*****	3.53	35.0	27.5	0.120
1455	235.	0.425	*****	*****	*****	3.61	35.0	27.5	0.121
1500	240.	0.427	*****	*****	*****	3.60	35.1	27.5	0.120
1505	245.	0.435	0.019	0.261	0.280	3.55	35.0	27.5	0.118

***** NO DATA TAKEN

---- DATA DISCARDED

? QUESTIONABLE DATA

OZONE COSAGE OF 0.10 = 41.80 PPM-MIN

OZONE COSAGE OF 0.08 = 46.32 PPM-MIN

NO2-PAN COSAGE OF 0.25 = 29.39 PPM-MIN

[illegible][illegible][illegible]

[illegible]

44-225 52-40X-508-11
105 64246
1976 Aug 24-25

2145	315	845	915	945	1015	1345	1115	1145	1215	1245	1315	1415
2146	316	846	916	946	1016	1346	1116	1146	1216	1246	1316	1416
2147	317	847	917	947	1017	1347	1117	1147	1217	1247	1317	1417
2148	318	848	918	948	1018	1348	1118	1148	1218	1248	1318	1418
2149	319	849	919	949	1019	1349	1119	1149	1219	1249	1319	1419
2150	320	850	920	950	1020	1350	1120	1150	1220	1250	1320	1420

CONFIDENTIAL (S)

[illegible]

SURROGATE RUN 223-U
GLASS CHAMBER
1976 OCT 5

LIGHTS ON 1215, INTENSITY = 100% OF MAXIMUM
39 GC SAMPLES TAKEN; CO FACTOR 1.9/1.01; PAN CALIBR 9; BRADY 1296
1215 PAN SAMPLE WAS TAKEN AT 1221
AT T=0; TOTAL NON-METHANE HC= 2346 PPBC; METHANE= 2950 PPB

CLOCK TIME	ELAPSED TIME (MIN)	OZONE (PPM)	NO (PPM)	NO2-PAN (PPM)	NOX-PAN (PPM)	CO (PPM)	PAN (PPM)	HCHO (PPM)	TS1 (DEG C)	REL HUM (%)
1215	0.	0.0	0.150	0.143	0.287	5.53	0.001	0.040	34.1	61.0
1230	15.	0.020	0.094	0.181	0.272	5.75	*****	*****	33.1	63.0
1245	30.	0.044	0.055	0.200	0.251	5.75	0.006	*****	33.8	63.0
1300	45.	0.071	0.038	0.208	0.237	5.72	*****	*****	33.6	62.5
1315	60.	0.098	0.028	0.200	0.224	5.72	0.011	0.063	33.6	62.0
1330	75.	*****	0.023	0.194	0.214	5.70	*****	*****	33.6	61.5
1345	90.	0.139	0.020	0.188	0.205	5.63	0.014	*****	33.7	61.0
1400	105.	0.159	0.017	0.181	0.194	5.61	*****	*****	33.8	60.5
1415	120.	0.181	0.015	0.173	0.185	5.57	0.018	0.095	34.0	59.5
1430	135.	0.203	0.024	0.157	0.176	5.56	*****	*****	34.1	59.0
1445	150.	0.222	0.012	0.161	0.165	5.52	0.021	*****	34.0	58.5
1500	165.	0.242	0.011	0.153	0.160	5.51	*****	*****	34.2	58.5
1515	180.	0.259	0.010	0.147	0.154	5.53	0.022	0.081	34.3	57.5
1530	195.	0.276	0.010	0.140	0.145	5.46	*****	*****	34.5	57.5
1545	210.	0.298	0.010	0.132	0.139	5.48	0.025	*****	34.5	57.0
1600	225.	0.318	0.007	0.125	0.130	5.43	*****	*****	34.6	56.5
1615	240.	0.337	0.012	0.124	0.131	5.39	0.027	0.024	34.7	56.0
1630	255.	0.354	0.007	0.114	0.116	5.43	*****	*****	34.8	56.0
1645	270.	0.374	0.006	0.105	0.105	5.42	0.031	*****	34.9	55.5
1700	285.	0.393	0.005	0.099	0.101	5.38	*****	*****	34.9	55.5
1715	300.	0.410	0.005	0.093	0.095	5.42	*****	0.051	34.8	55.0
1730	315.	0.427	0.005	0.088	0.089	5.38	*****	*****	34.9	55.0
1745	330.	0.445	0.005	0.081	0.081	5.35	*****	*****	*****	55.0
1800	345.	0.462	0.007	0.074	0.075	5.39	*****	*****	*****	54.5
1815	360.	0.479	0.002	0.068	0.069	5.37	0.039	*****	34.7	55.0

***** NO DATA TAKEN ----- DATA DISCARDED ? QUESTIONABLE DATA

OZONE DOSEAGE GT 0.10 = 53.58 PPM-MIN
OZONE DOSEAGE GT 0.09 = 64.66 PPM-MIN
NO2-PAN DOSEAGE GT 0.25 = 3.0 PPM-MIN

1977 MAR 15

GLDGCATE 223-U
GLASS CHAMBER
1976 OCT 5

PCBP TEMPERATURE STABILITY ON POROPAK N INSTRUMENT
1345-GUS SAMPLE USED ON POROPAK N
ACETALDEHYDE, PROPIONALDEHYDE, ACETONE, BUTYRALDEHYDE AND MEK FROM C-600
TOLUENE AND M-XYLENE FROM 3P

CLOCK TIME ELAPSED TIME(MIN)	CONCENTRATIONS (PPB)															
	1015	1132	1215	1230	1245	1300	1315	1330	1345	1400	1415	1430	1445	1500	1530	165
METHANE	-120	-43	0	15	30	45	60	75	90	105	120	135	150	165		
	PPBC	1120	***	2950	***	***	2920	***	***	***	2880	***	***	***	***	***
ETHANE	1.3	4.4	***	***	***	***	***	***	30.1	***	27.5	***	***	***	***	***
	PPBC	2.6	***	***	***	***	***	***	61.4	***	55.0	***	***	***	***	***
ETHANE	4.2	***	***	***	***	***	***	***	81.9	***	81.0	***	***	***	***	***
	PPBC	8.4	***	***	***	***	***	***	170	***	162	***	***	***	***	***
ACETYLENE (POROPAK N)	2.4	***	***	***	***	***	***	***	92.5	***	38.6	***	***	***	***	***
	PPBC	4.8	***	***	***	***	***	***	86.6	***	77.2	***	***	***	***	***
PROPANE	4.3	***	20.0	***	19.6	***	18.9	***	***	***	13.8	***	***	***	16.2	***
	PPBC	12.9	60.0	***	58.6	***	56.7	***	***	***	56.4	***	***	***	54.6	***
PROPENE	0.7	12.9	12.9	***	8.7	***	6.5	***	***	***	4.0	***	***	***	2.6	***
	PPBC	2.1	38.7	38.7	***	26.1	19.5	***	***	***	12.0	***	***	***	7.8	***
ISOBUTANE	0.1	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***
	PPBC	0.4	***	***	***	***	***	***	***	***	***	***	***	***	***	***
N-BUTANE	3.5	198	196	***	186	***	***	***	***	***	171	***	***	***	164	***
	PPBC	14.0	790	784	***	744	***	***	***	***	684	***	***	***	656	***
ACETYLENE (DMS)	2.5	42.4	42.5	***	42.5	***	42.5	***	***	***	41.4	***	***	***	39.2	***
	PPBC	5.0	86.8	85.0	***	85.0	85.0	***	***	***	82.8	***	***	***	73.4	***
TRANS-2-BUTENE	0.0	0.0	0.0	***	0.3	***	0.0	***	***	***	0.0	***	***	***	0.0	***
	PPBC	0.0	3.2	3.2	***	1.2	0.0	***	***	***	0.0	***	***	***	0.0	***
ISOPENTANE	0.3	0.7	0.2	***	1.0	***	1.1	***	***	***	1.1	***	***	***	1.2	***
	PPBC	1.5	3.5	4.5	***	5.0	5.5	***	***	***	5.5	***	***	***	6.0	***
CIS-2-BUTENE	0.0	14.8	14.6	***	5.2	***	1.7	***	***	***	0.0	***	***	***	0.0	***
	PPBC	0.0	59.2	58.4	***	20.8	6.8	***	***	***	0.0	***	***	***	0.0	***
N-PENTANE	0.0	0.2	0.3	***	0.3	***	0.5	***	***	***	0.5	***	***	***	***	***
	PPBC	0.0	1.0	1.5	***	1.5	2.5	***	***	***	2.5	***	***	***	***	***
2,3-DIMETHYL BUTANE	0.0	109	110	***	99.5	***	93.1	***	***	***	84.6	***	***	***	79.5	***
	PPBC	0.0	652	658	***	597	559	***	***	***	509	***	***	***	477	***
2-METHYL BUTENE-2	0.0	16.2	16.6	***	2.4	***	0.0	***	***	***	0.0	***	***	***	0.0	***
	PPBC	0.0	16.2	16.6	***	2.4	0.0	***	***	***	0.0	***	***	***	0.0	***

1977 MAR 18

SURROGATE 223-U
GLASS CHAMBER
1976 OCT 5

CLOCK TIME	1015	1132	1215	1230	1245	1300	1315	1330	1345	1400	1415	1430	1445	1500
ELAPSED TIME(MIN)	-120	-43	0	15	30	45	60	75	90	105	120	135	150	165
PPBC	0.0	01.0	03.0	04.5	06.0	07.5	09.0	10.5	12.0	13.5	15.0	16.5	18.0	19.5
ACETALDEHYDE	2.8	5.6	8.4	11.2	14.0	16.8	19.6	22.4	25.2	28.0	30.8	33.6	36.4	39.2
PROPIONALDEHYDE	0.2	0.6	1.0	1.4	1.8	2.2	2.6	3.0	3.4	3.8	4.2	4.6	5.0	5.4
ACETONE	0.7	1.4	2.1	2.8	3.5	4.2	4.9	5.6	6.3	7.0	7.7	8.4	9.1	9.8
METHYL ETHYL KETONE	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.7	3.0	3.3	3.6	3.9	4.2
TOLUENE	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8
META-XYLENE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BUTYRALDEHYDE	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
DICHLORO DIFLUOROMETHANE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOTAL HC PPBC	1178.3	2241.5	3304.7	4367.9	5431.1	6494.3	7557.5	8620.7	9683.9	10747.1	11810.3	12873.5	13936.7	15000.0
TOTAL NON-METHANE HC	58.3	116.6	174.9	233.2	291.5	349.8	408.1	466.4	524.7	583.0	641.3	699.6	757.9	816.2
TOTAL SURROGATE	1236.6	2358.1	3479.6	4591.1	5722.6	6844.1	7969.6	9096.1	10221.6	11348.1	12473.6	13600.1	14726.6	15856.2

1977 MAR 16

1515	1530	1545	1600	1615	1630	1645	1700	1715
180	195	210	225	240	255	270	285	300

CONCENTRATIONS (PPB)

146

1977 MAR 18

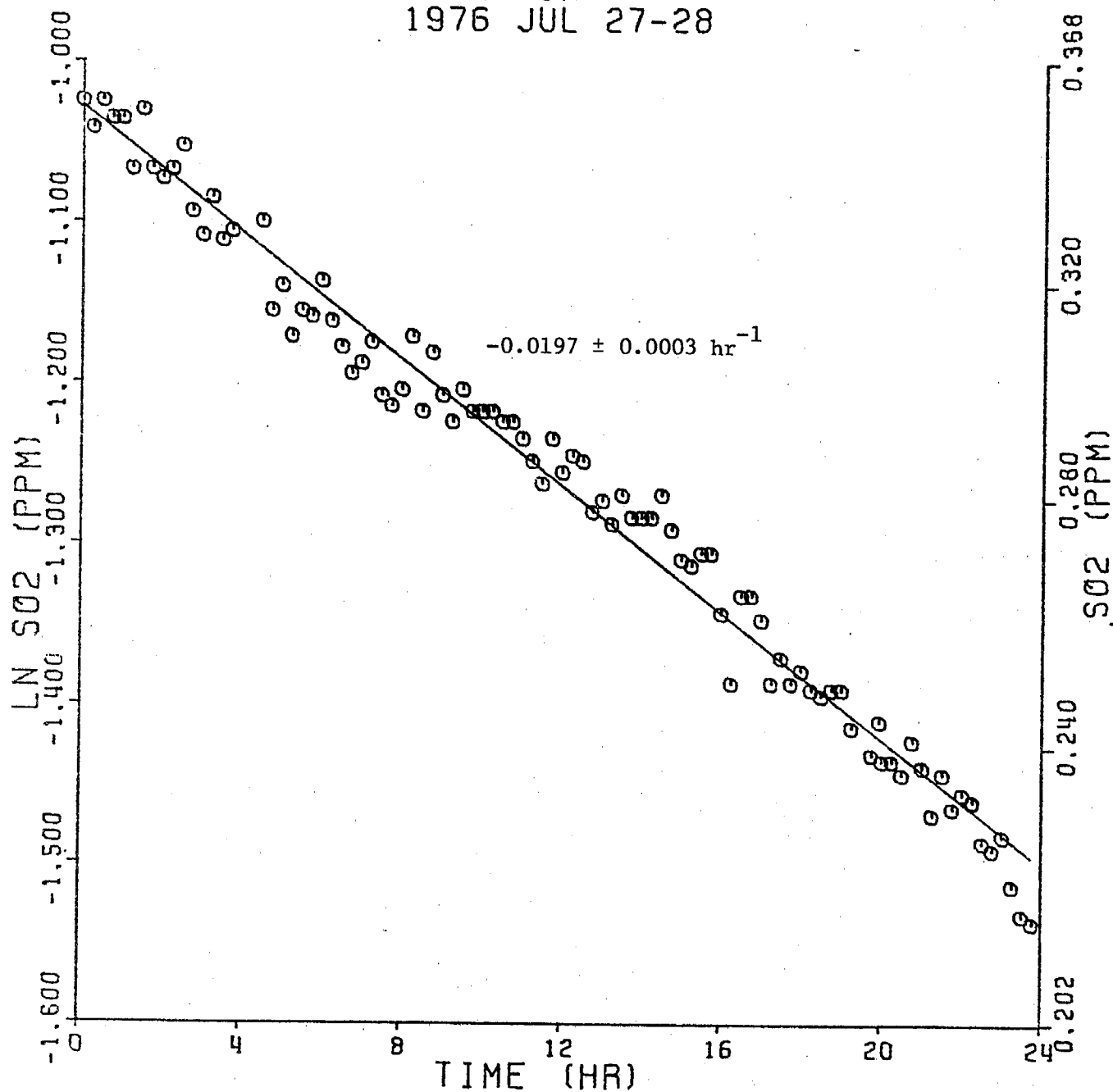
SURCGATE 223-U
GLASS CHAMBER
1976 OCT 5

CLOCK TIME	1515	1530	1545	1600	1615	1630	1645	1700	1715
ELAPSED TIME(MIN)	180	195	210	225	240	255	270	285	300
ACETONE	PPBC	***	***	***	38.0	***	***	***	***
		***	***	***	114	***	***	***	***
METHYL ETHYL KETONE	PPBC	***	***	***	9.7	***	***	***	18.2
		***	***	***	38.8	***	***	***	72.8
TOLUENE	PPBC	10.9	***	***	***	10.7	***	***	10.2
		76.3	***	***	***	75.1	***	***	71.6
META-XYLENE	PPBC	17.7	***	***	***	12.5	***	***	9.4
		142	***	***	***	00.0	***	***	75.1
BUTYRALDEHYDE	PPBC	***	***	***	***	2.2	***	***	2.6
		***	***	***	***	8.8	***	***	13.4
DICHLOROPIC DIFLUOROMETHANE	PPBC	***	330	***	326	***	322	***	311
		***	330	***	326	***	322	***	311
TOTAL HC PPBC	3304.3	***	***	***	3438.7	***	***	***	4713.6
TOTAL NON-METHANE HC	494.3	1339.3	63.0	1205.5	628.7	1177.0	0.0	0.0	1522.9
TOTAL SURCGATE	494.3	1330.3	83.0	1196.0	455.1	1166.5	***	***	1412.8

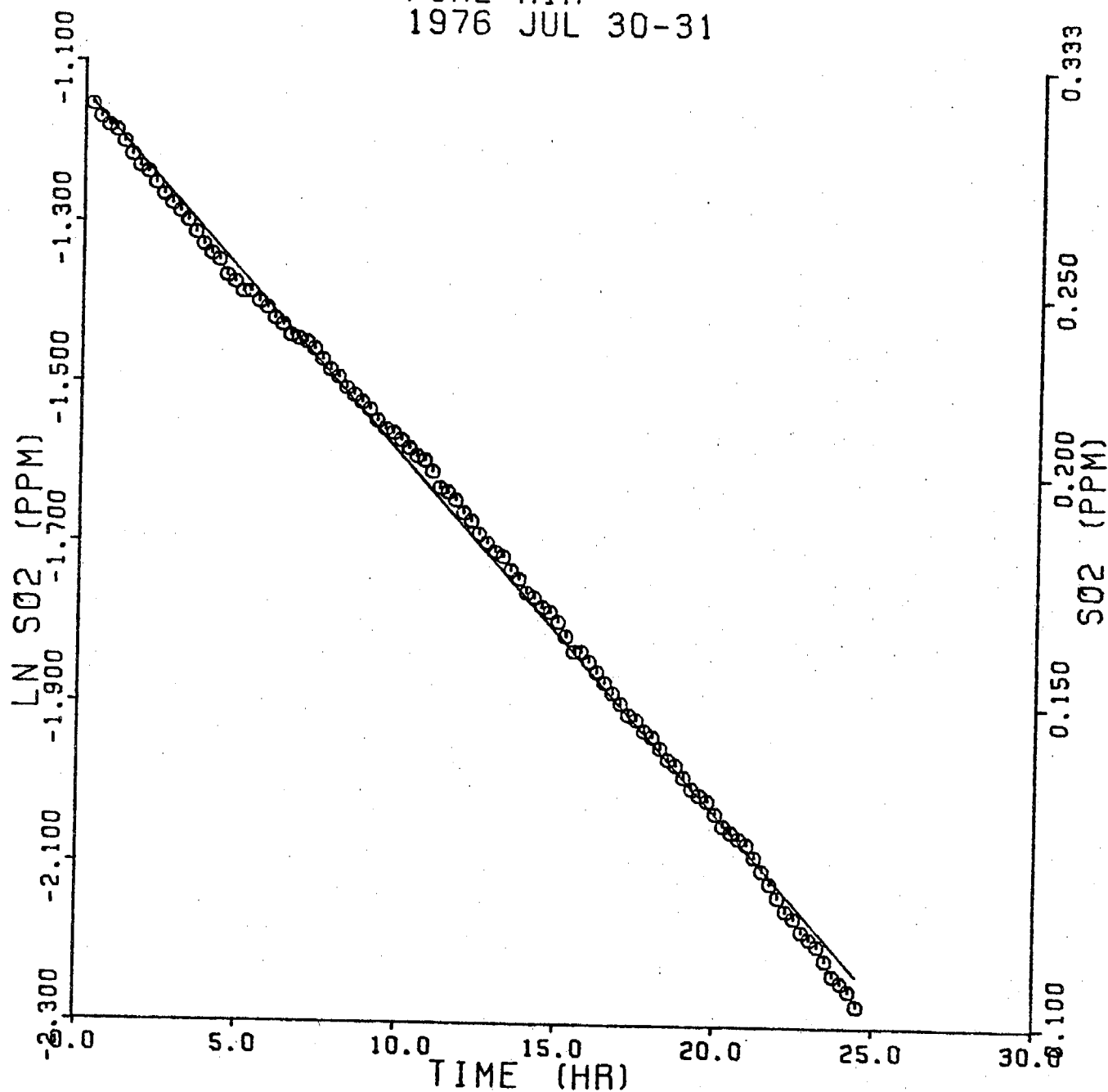
APPENDIX C

Plots of $\ln \text{SO}_2$ vs. time for
AGC Runs 216 through 222

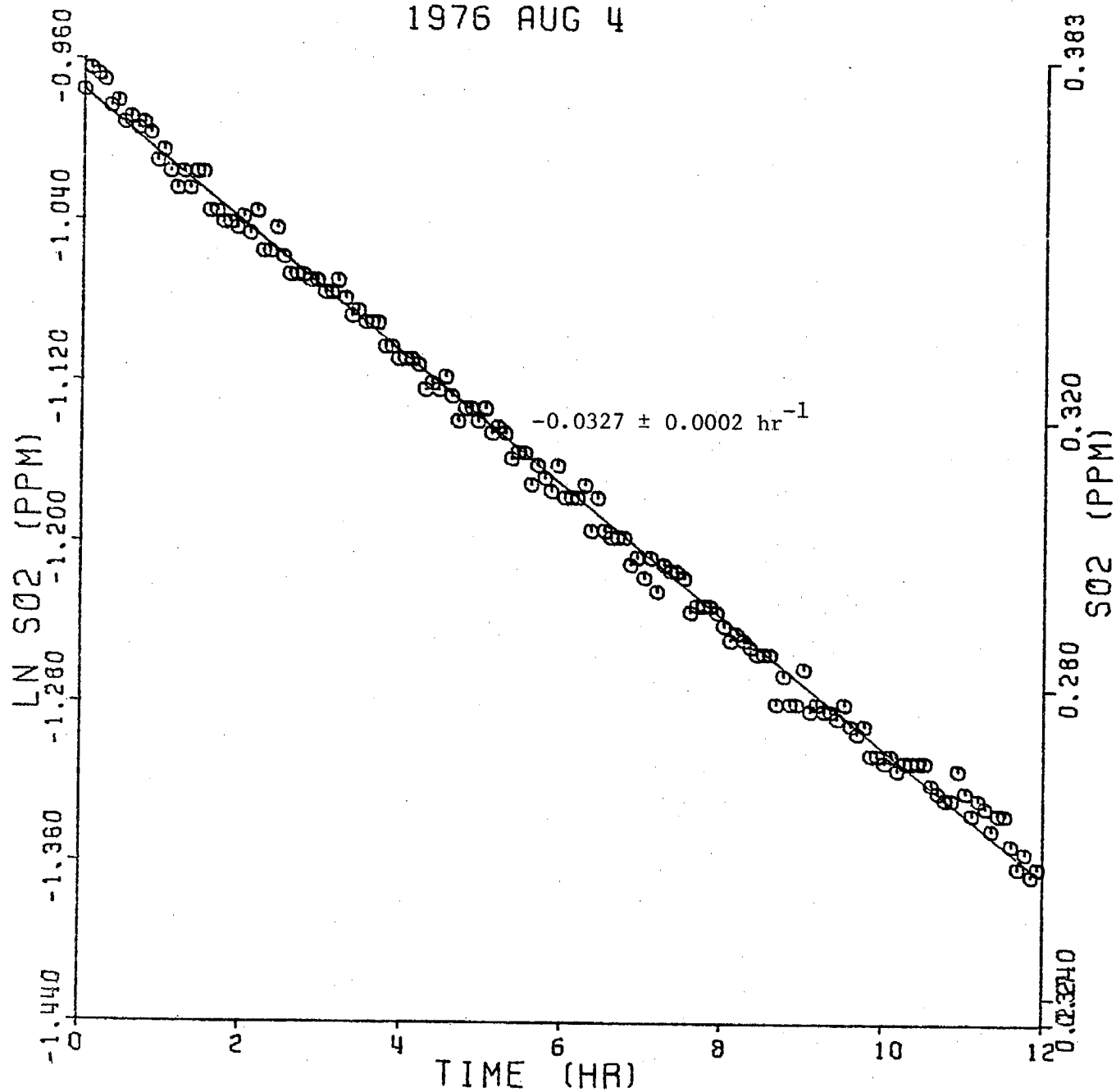
AGC-216-1-3
SO2 DARK DECAY, 2% RH
PURE AIR
1976 JUL 27-28



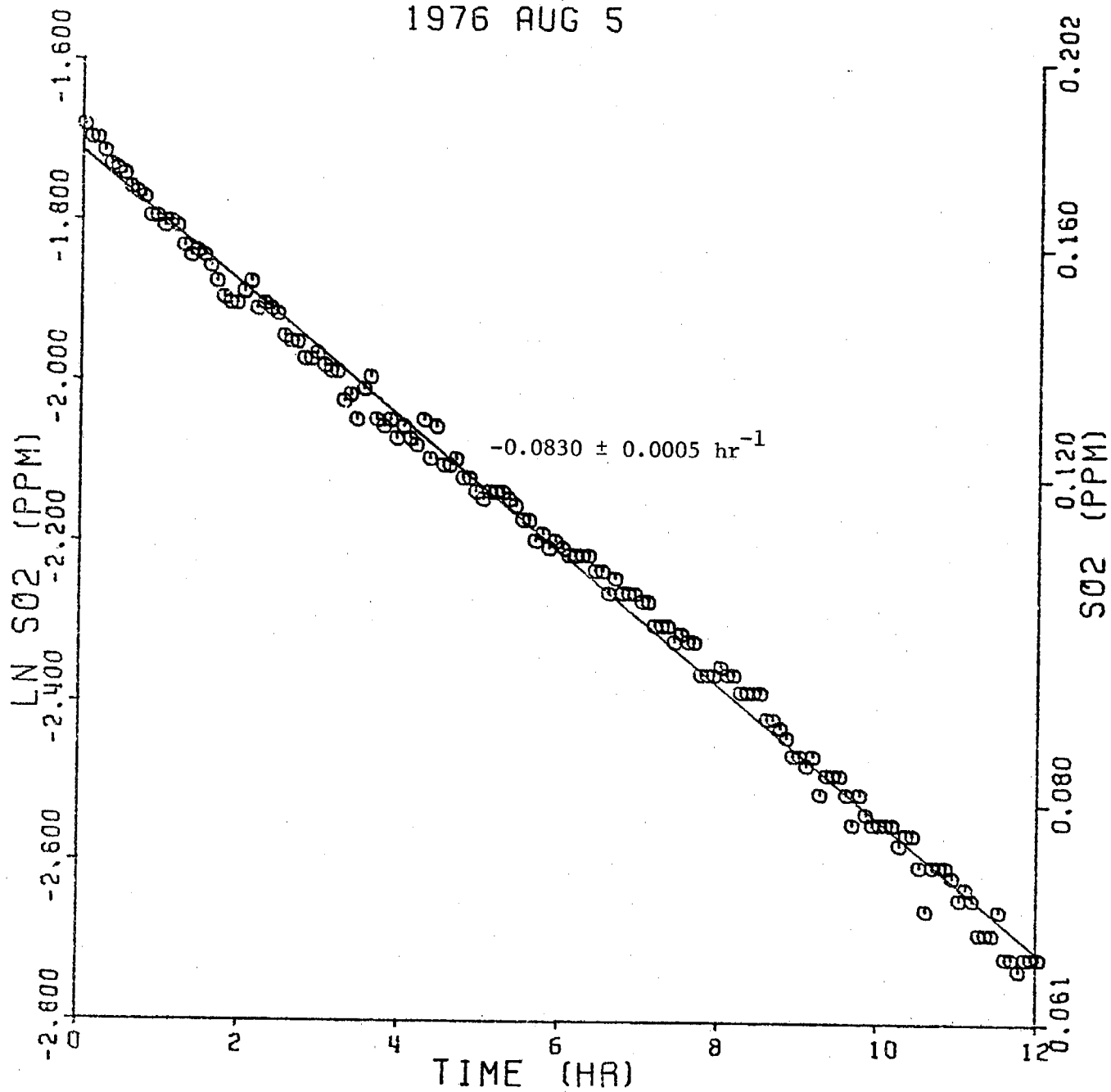
AGC-217-1-2
SO₂ LIGHT DECAY, 15% RH
PURE AIR
1976 JUL 30-31



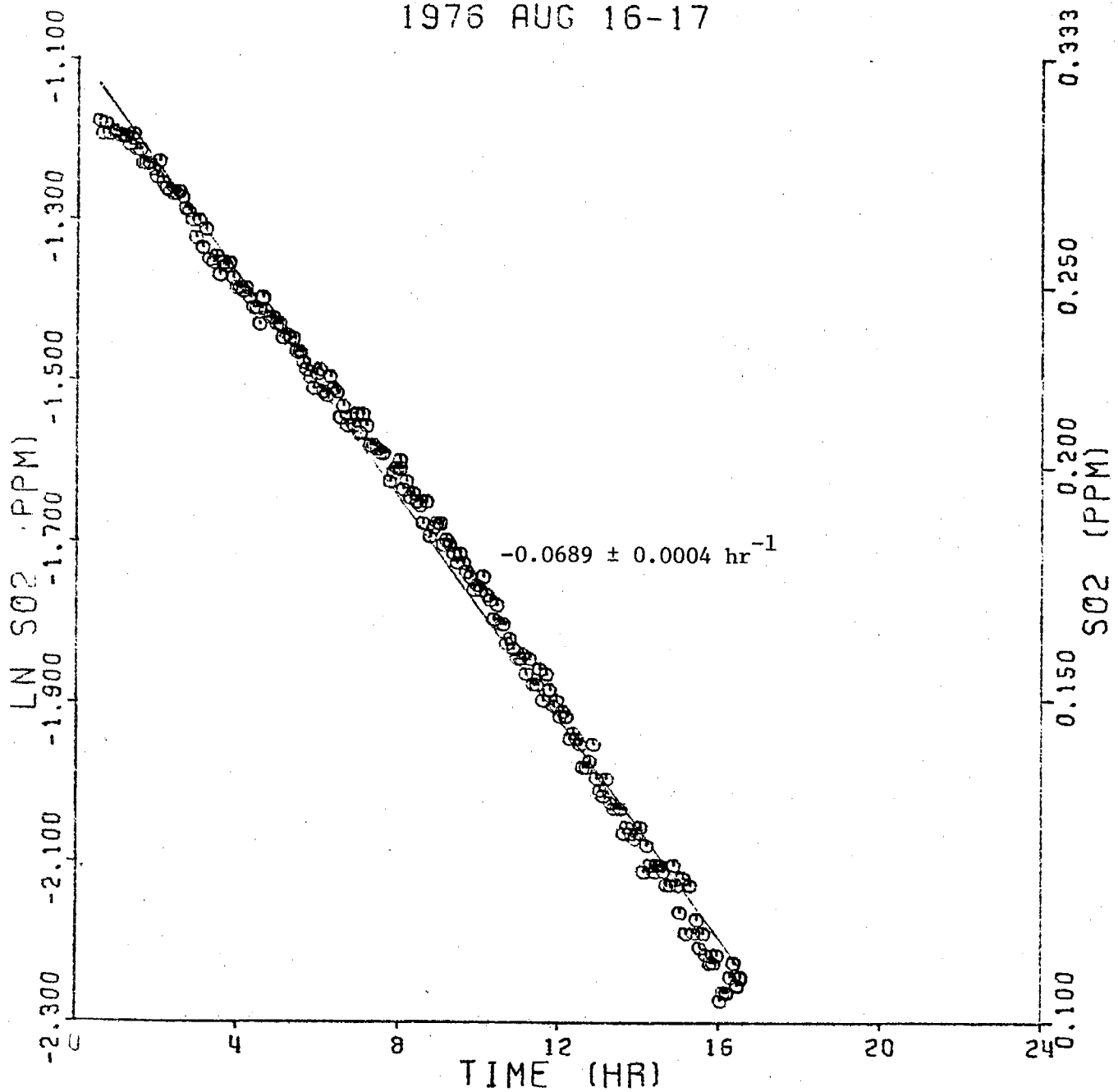
AGC-218-1-3
SO2 DARK DECAY, 40% RH
PURE AIR
1976 AUG 4



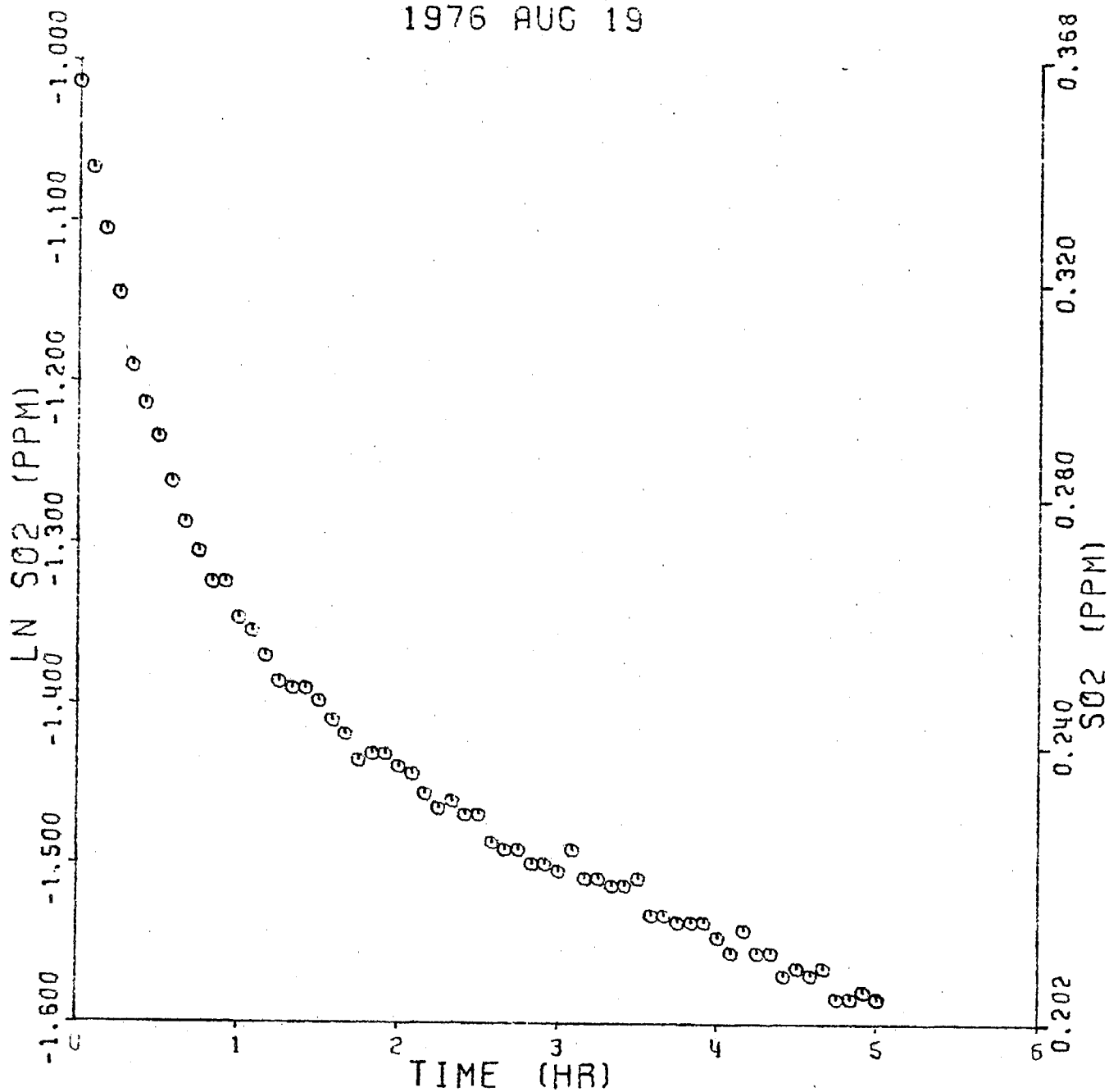
AGC-218-7-9
SO2 LT DECAY, 40% RH
PURE AIR
1976 AUG 5



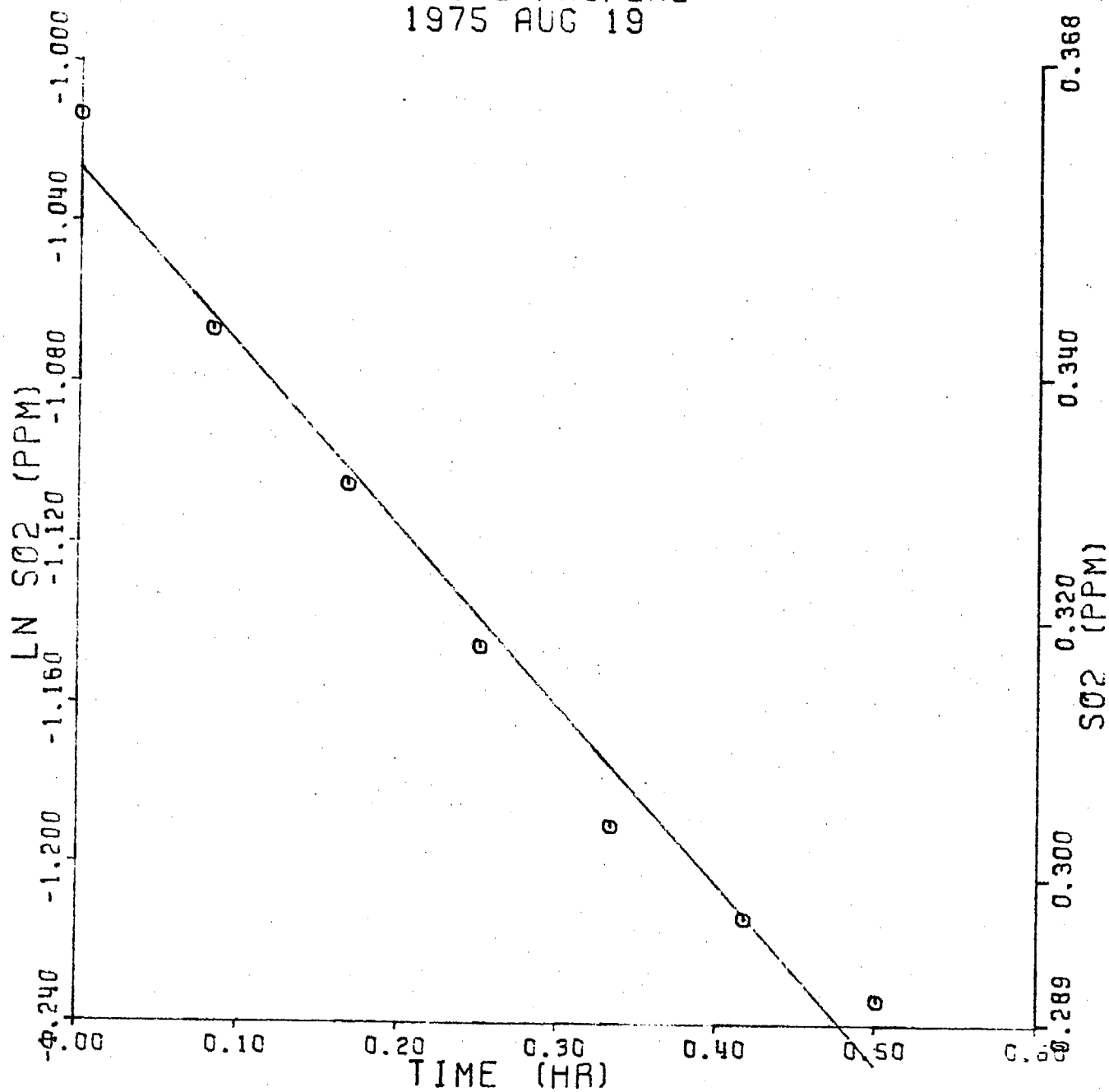
AGC 219-1-5
SO2 DARK DECAY. 80% RH
PURE AIR
1976 AUG 16-17



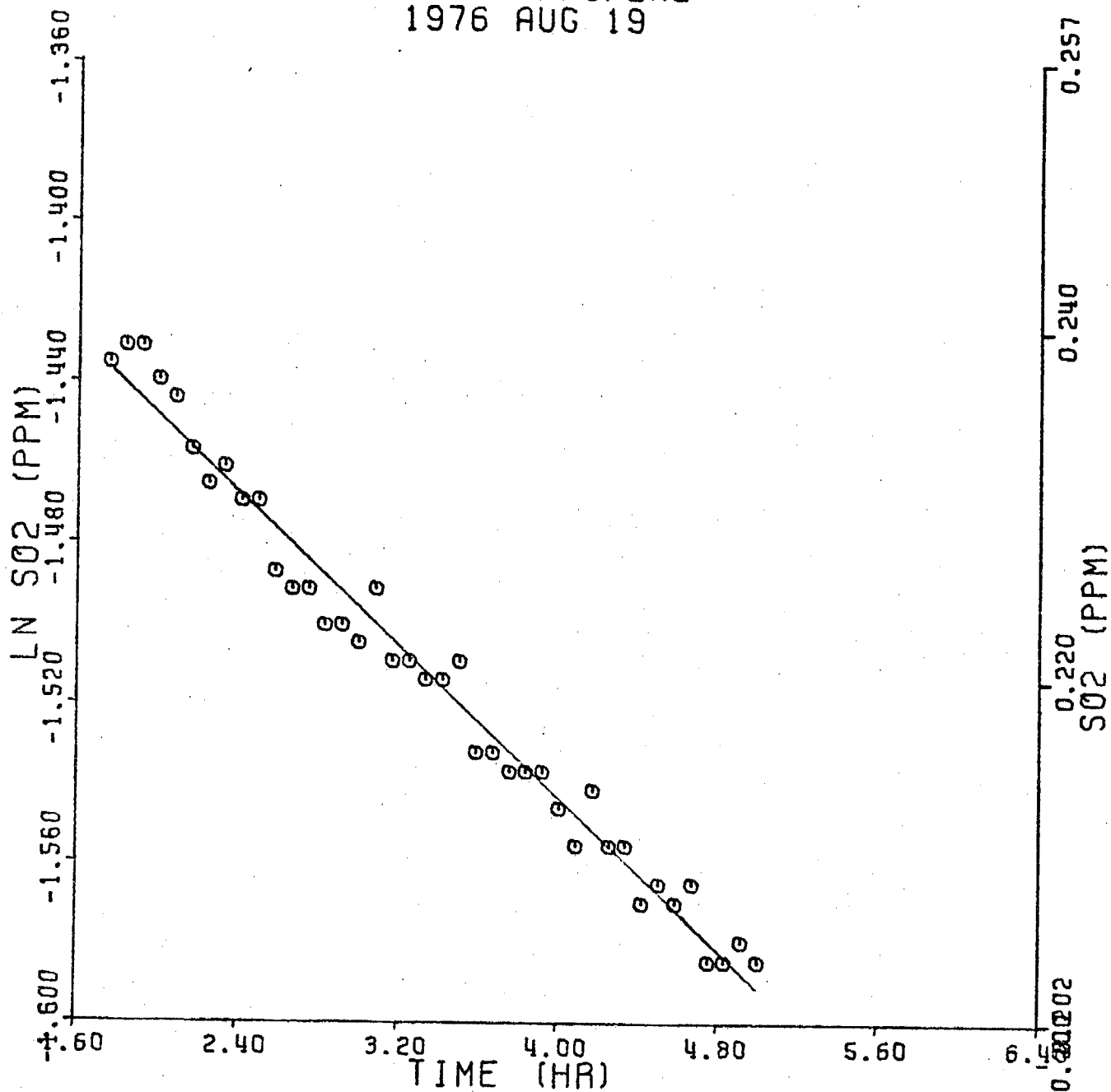
AGC-220-1-2
SO2 DARK DECAY. 40% RH
OZONE-PROPENE
1976 AUG 19



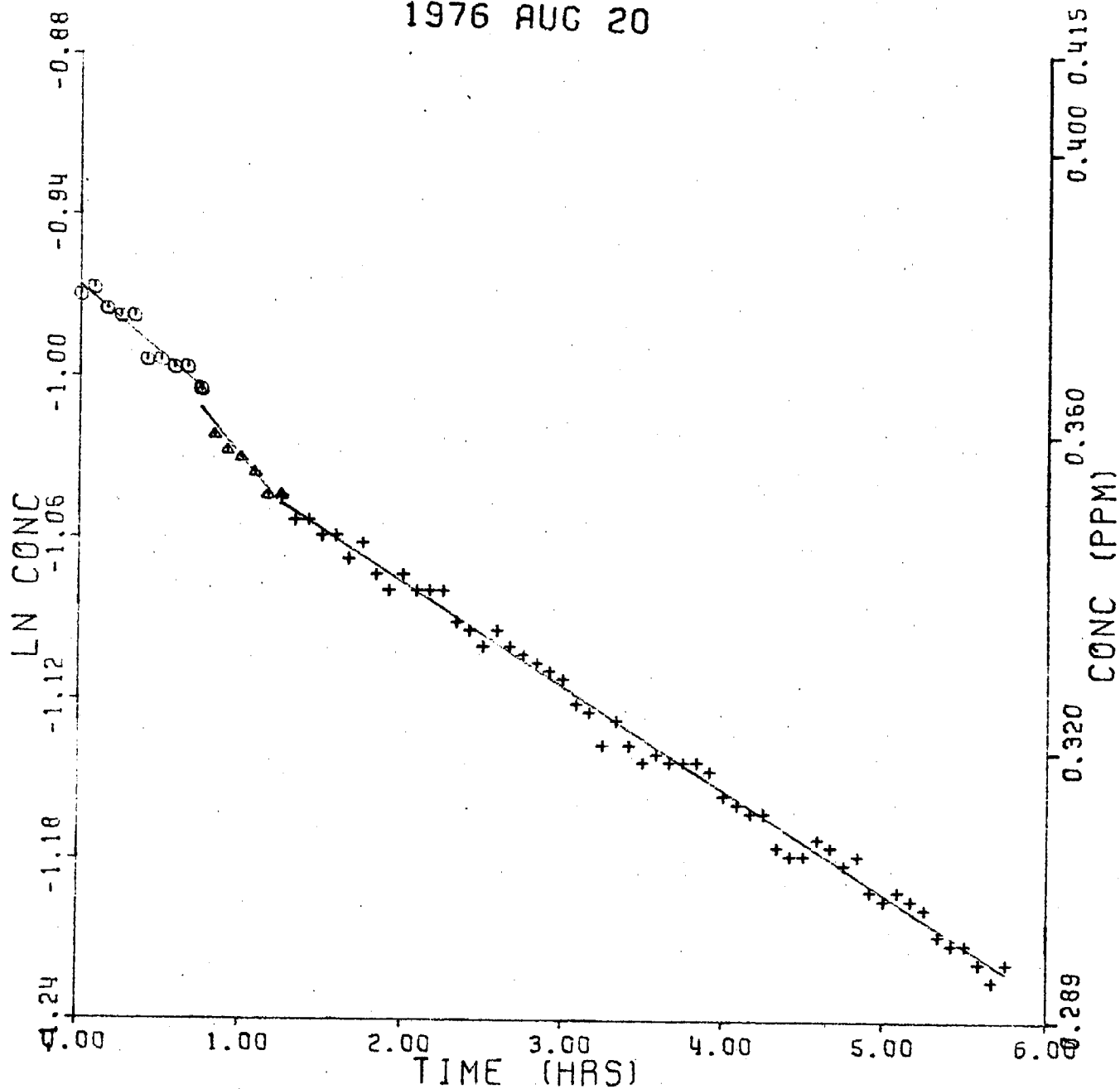
AGC-220 0.0-0.5 HOURS
 SO2 DARK DECAY, 40% RH
 OZONE-PROPENE
 1975 AUG 19



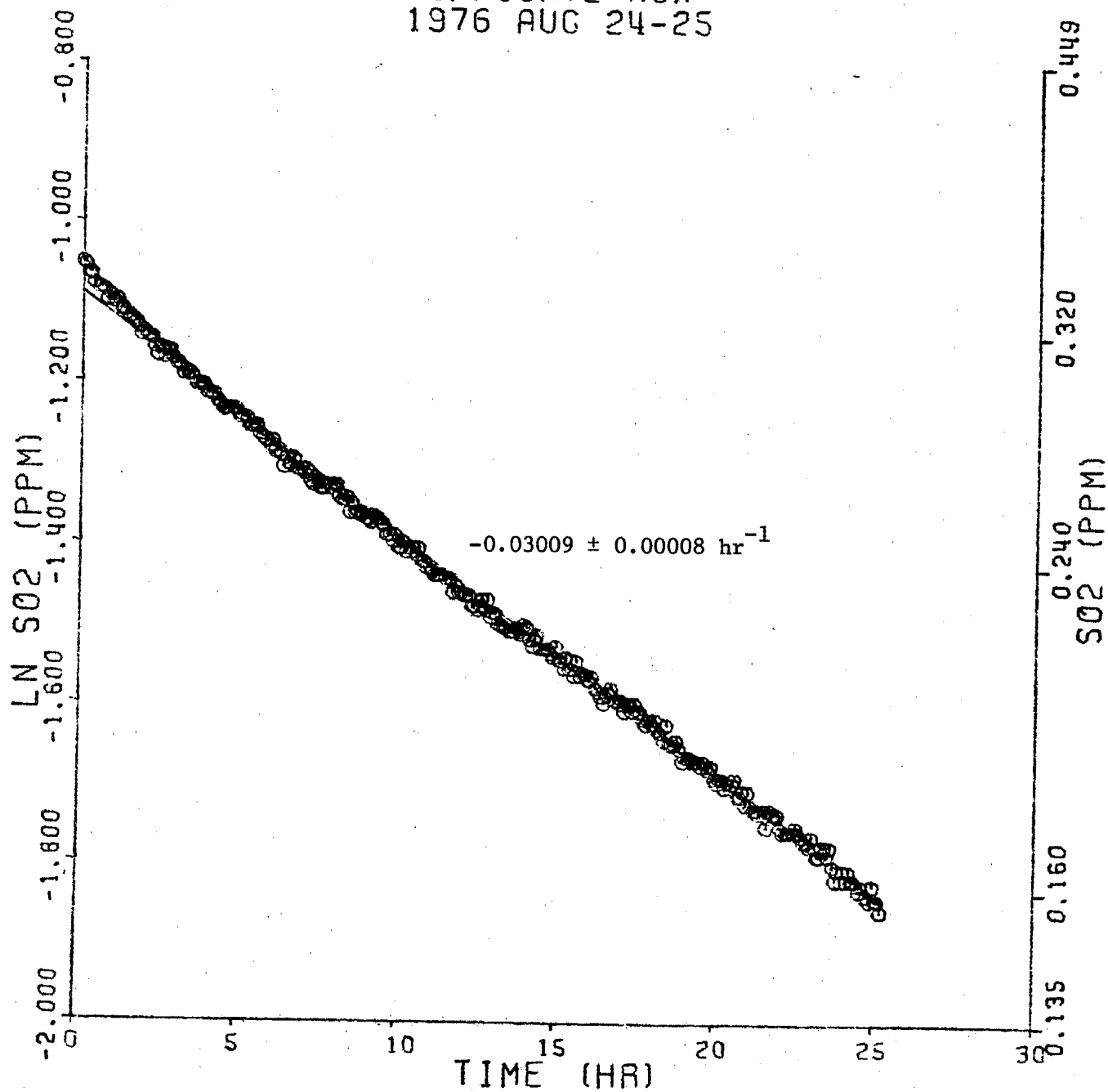
AGC-220 1.75-5.0 HOURS
 SO2 DARK DECAY, 40% RH
 OZONE-PROPENE
 1976 AUG 19



ACC-221-1-2
SO2 DARK DECAY, 40% RH
ADD OZONE 0.80 HRS
1976 AUG 20



AGC-222-1-7
SO2 DARK DECAY, 40% RH
SURROGATE-NOX
1976 AUG 24-25



AGC-222-8-9
SO2 LIGHT DECAY. 30% RH
SURROGATE-NOX
1976 AUG 25

